AFWAL-TR-85-4079

ADA160931O

X-RAY ANALYSIS SOFTWARE:

OPERATION AND THEORY INVOLVED IN PROGRAM "DIFF"

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June 1985

INTERIM REPORT FOR PERIOD MAY 84 - MARCH 85

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UDR-TR-85-50	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-85-4079
6a. NAME OF PERFORMING ORGANIZATION University of Dayton Research Institute 6b. OFFICE SYMBOL (*If applicable*)	7a. NAME OF MONITORING ORGANIZATION Materials Laboratory (AFWAL/MLBC)
6c. ADDRESS (*City, State and ZIP Code*) 300 College Park Avenue Dayton, OH 45469	7b. ADDRESS (*City, State and ZIP Code*) Air Force Wright Aeronautical Laboratories AFSC Wright-Patterson AFB, OH 45433
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Materials Laboratory 8b. OFFICE SYMBOL (*If applicable*) AFWAL/MLBC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F33615-84-C-5070
8c. ADDRESS (*City, State and ZIP Code*)	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. 62102F; PROJECT NO. 2419; TASK NO. 241901; WORK UNIT NO. 24190168
11. TITLE (*Include Security Classification*) X-RAY ANALYSIS SOFTWARE: Operation (cont'd)	
12. PERSONAL AUTHOR(S) David P. Anderson	
13a. TYPE OF REPORT Interim 13b. TIME COVERED FROM May 84 TO Mar 85	14. DATE OF REPORT (*Yr., Mo., Day*) June 1985 15. PAGE COUNT 105
16. SUPPLEMENTARY NOTATION	

17. COSATI CODES			18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
FIELD	GROUP	SUB. GR.	X-ray diffraction, Crystallites, Polymers, Curve Fitting, Crystallinity

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

Program "DIFF" described in this report is a combination of several different software packages available in the public domain as well as specific modifications made by the members of the Morphology Group, AFWAL/MLBP. Desper's x-ray reduction programs (Reference 1) with several additional analysis subroutines formed the basic program until several major additions were incorporated. The addition of curve fitting (References 2 and 3), line broadening analysis (Reference 4), and degree of crystallinity subroutines (References 5 and 6) changed the program's operation and appearance significantly. Recent additions of newer crystallographic advances and changes in the program operation stimulated the documenting of this software along with documentation of equipment in this area (References 7 and 8). While individual pieces of software and the basic techniques incorporated into the program are described elsewhere, this report brings together all of the operation and theory currently used in the program.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☒ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL J. M. Whitney	22b. TELEPHONE NUMBER (*Include Area Code*) (513) 255-6685 22c. OFFICE SYMBOL AFWAL/MLBM

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

11. (Continued)

and Theory Involved in Program "DIFF"

FOREWORD

This Interim Technical Report was prepared by the University of Dayton Research Institute, Dayton, Ohio under United States Air Force Contract No. F33615-84-C-5070, Project No. 2419, Task No. 241901, Work Unit No. 24190168. It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. J. M. Whitney as the Project Engineer.

This report covers work conducted from May 1984 through March 1985.

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SECTION 1

INTRODUCTION

The program, DIFF, is designed to except x-ray diffraction data from a variety of sources and analyze that data. Besides corrections to the intensities, that data may need to be plotted, or the scientist may want any of the information contained in a diffraction scan: degree of cryatallinity, crystallite sizes, unit cell and unit cell dimensions, crystal strain, etc.

This report is divided into two major areas: program theory and program operation. Anyone just interested in knowing how to use the program, only has to read the Operation section. If one is interested in the basic theory and equations used then the Theory section will describe the various parts of the program and give references for further reading.

Program DIFF is a Fortran 77 program adapted to run on the PRIME 850 computer (FTN77 compiler) of the Air Force Materials Laboratory. This program is designed to run interactively or as a batch job (albeit with fewer of the options available). The program currently resides in the ADAMS>DAVE user file sub-directory used by the AFWAL/MLBP Morphology Group and other morphologists.

This program contains several analysis options for x-ray data including parts of Desper's x-ray data reduction programs [1] with the addition of curve fitting [2] and [3], line broadening analysis [4], and degree of crystallinity subroutines [5] and [6]. Data from several sources can be analyzed once that data is in a computer data-file [7] and [8].

SECTION 2

PROGRAM THEORY

2.1 INTENSITY CORRECTIONS

The observed diffracted x-ray intensity (I_{obs}) is related to the "ideal" intensity or the structure factor, $|F|$ by the following equation [9]:

$$I_{obs} = P \cdot L \cdot j \cdot A \cdot |F|^2 + I_{bkg} + I_{inc} \qquad (1)$$

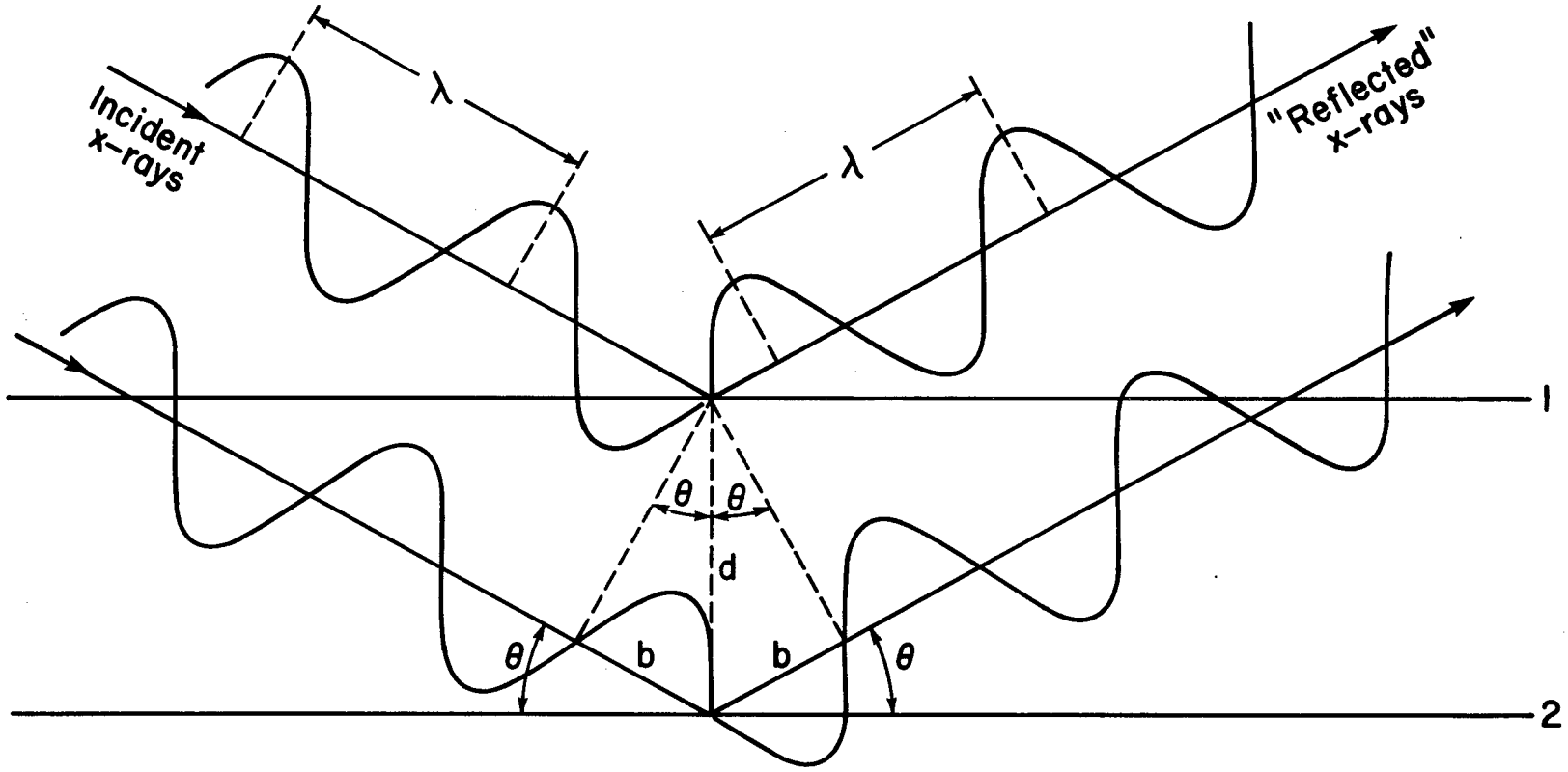
where P = the polarization factor,
L = the Lorentz correction,
j = the multiplicity factor,
A = the absorption correction,
$|F|$ = the structure factor,
I_{bkg} = background or air scattering intensity, and
I_{inc} = incoherent or Compton's scattering intensity.

Each of these factors will be discussed in the sections below. Not all of these factors need be accounted for in the final analysis depending on what information is needed and what experiments have been performed.

The angular position (2θ) of the diffracted intensity is dependent on the spacing of the crystal lattice planes according to Bragg's law [10]:

$$n\lambda = 2\, d \sin \theta. \qquad (2)$$

The d-spacing represents the lattice spacing where constructive interference occurs with the diffracted beams as in Figure 1. The reciprocal of the d-spacing is the reciprocal lattice vector: $s = 1/d$.



CONSTRUCTIVE INTERFERENCE WHEN:

$$n\lambda = 2b = 2d \sin\theta$$

Figure 1. Bragg's law geometry.

2.1.1 Polarization Factor

The polarization factor takes into account the loss of intensity resulting from the fact that the x-rays are polarized when they are diffracted. This polarization factor is dependent on the diffraction angle according to Equation 3.

$$P = \frac{1 + \cos^2 2\theta}{2} \tag{3}$$

When x-rays are diffracted through a crystal monochromator to obtain a narrow wavelength beam, then the polarization due to that crystal must be accounted for as well as the sample polarization. Equation 4 describes the angular dependence of the polarization factor when the crystal monochromator diffraction plane is perpendicular to the sample diffraction plane. This is the case with the Picker FACS-1 diffractometer which is why this equation is used by the program. The equation takes other forms when the sample and monochromator diffraction planes are oriented differently.

$$P = \frac{\cos^2 2\theta' + \cos^2 2\theta}{1 + \cos^2 2\theta'} \tag{4}$$

The polarization numbers given in the Predata section which follow "POLM" are the $\cos^2 2\theta'$ values for the particular monochromator and wavelength used from which P values are calculated.

2.1.2 Lorentz Correction

Diffracted x-rays are visible only on the "sphere of reflection" and the Lorentz correction accounts for the intensity not visible in the observed intensity. This correction is both angularily dependent and wavelength dependent. While the Lorentz and Polarization factors are often combined in tables for a particular method these factors are separated in this program because of the variety of forms the Lorentz

correction takes depending on the type of crystals and their orientation in the sample. For random powders of small crysals or unoriented bulk polymer crystals this correction is proportional to the square of the reciprocal space vector, or the so called Ruland correction [5]. This correction gets very large at high angles and is not always applied when plotting intensities:

$$L = \sin^2\theta \cos\theta . \qquad (5)$$

2.1.3 Multiplicity Factor

The multiplicity factor, j, is equal to the number of reflection planes contributing to the intensity at a particular Bragg angle. A knowledge of the number of planes with the same or nearly same spacing which contribute to a diffraction peak help determine the type of crystals doing the diffraction.

2.1.4 Absorption Correction

The interaction of x-rays with matter produce more than diffraction or scattering, matter can also absorb the x-rays. The amount of absorption is dependent on the number and types of atoms the x-ray beam encounters in the sample which is dependent on sample composition, density, and thickness. The actual thickness of sample through which the x-rays pass is dependent on the diffraction collection geometry. The absorption in fibers is dependent on many factors and the program uses a look-up table from the International Tables for X-Ray Crystallography [11a] to determine the absorption factor. The fiber elemental composition and μR value (R is the fiber radius) are needed for this determination.

The absorption in films is relatively easy to calculate depending on the collection geometry. The most commonly used geometry for polymer film sample is the Symmetrical Transmission Geometry shown in Figure 2. To calculate the absorption correction one must assume an incident beam

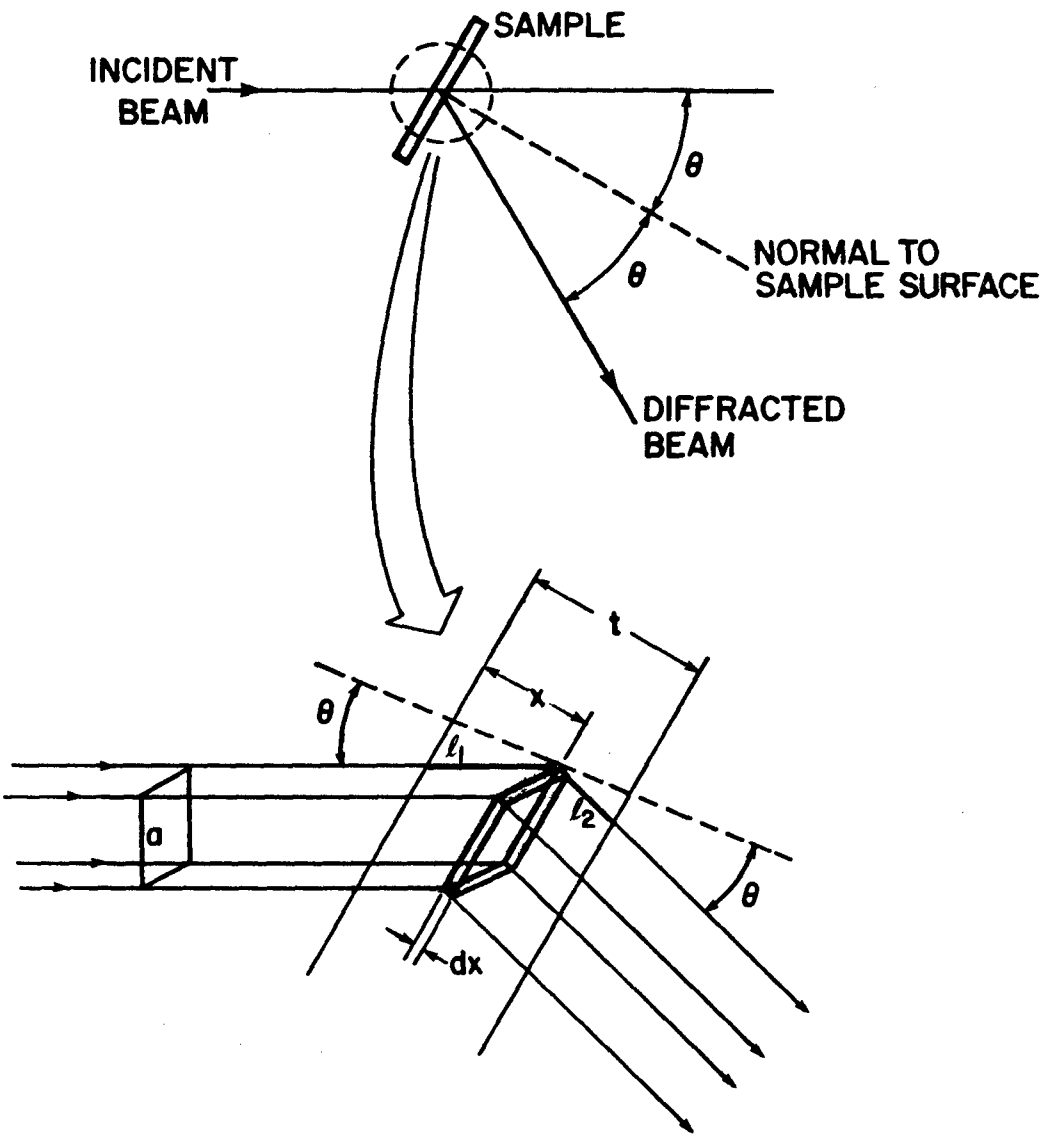


Figure 2. Symmetric transmission geometry.

cross-sectional area, a, striking a volume element at depth, x, of: a $\sec\theta$ dx. The linear absorption coefficient, μ (calculated from tables from the International Tables for X-Ray Crystallography [11b]), reduces the intensity according to the exponential equation:

$$I = I_o \exp[-\mu t] \tag{6}$$

For the above volume element both l_1 and l_2 are added to give an intensity at 2θ of dI:

$$dI = I_o \, a \sec\theta \exp[-\mu(l_1 + l_2)] \, dx$$

$$= I_o \, a \sec\theta \exp[-\mu t \sec\theta] \, dx \tag{7}$$

The total intensity at 2θ is then:

$$I = \int_o^t dI$$

$$= I_o \, a \sec\theta \int_o^t \exp[-\mu t \sec\theta] \, dx$$

$$= I_o \, a \, t \sec\theta \exp[-\mu t \sec\theta] \tag{8}$$

The angular dependence of the absorption is simply the ratio of intensities at Ø degrees to 2θ:

$$\frac{I_{\emptyset o}}{I_{2\theta}} = \frac{I_o \, a \, t \exp[-\mu t]}{I_o \, a \, t \sec\theta \exp[-\mu t \sec\theta]}$$

$$= \frac{\exp[-\mu t \, (1 - \sec\theta)]}{\sec\theta} \tag{9}$$

A more general equation for deviations from the symmetric transmission geometry is in the program, as well as a similar equation for normal transmission. The type of data collection defines which equation should be used, which the program chooses from the predata information.

Equation 6 is also used to measure film specimen's μt values by allowing that specimen to absorb x-rays directly in front of the detector and getting relative intensity values.

2.1.5 Structure Factor

The structure factor for a particular hkl reflection is the "ideal" intensity of that reflection. It is a complex sum of all the atoms' spherical scattering factors (f_n) and position terms:

$$F(hkl) = \sum_{n=1}^{N} f_n \exp\{ 2\pi i (h x_n + k y_n + l z_n)\} \qquad (10)$$

where h,k,l are the reflection's Miller's indices and

x_n, y_n, z_n are the unit cell fractional coordinates for the n-th atom of a total of N.

F is the Fourier transform function of f and vice-versa.

2.1.6 Background Intensity

The background is simply the intensity which reaches the detector as a result of the main beam being scattered by air; also called the air scattering. Within the program the background scan is normalized to account for the absorption of the main beam by the sample.

2.1.7 Incoherent Scattering Intensity

Incoherent scattering is sometimes called Modified scattering or Compton's scattering. It is called Modified scattering because these are x-rays which have interacted with electrons in atoms such that energy is lost from the x-rays (the wavelength of Incoherent scattering is lower than Coherent scattering). Because of the finite size of atoms, the phase difference between scattered waves increases with increased Bragg angle. This results in a decrease in Coherent

scattering and an increase in Incoherent scattering as 2θ increases. The most efficient means of elimnating incoherent scattering is to use a diffracted beam monochromator, but not all machines are equiped to do this.

In the program, the incoherent scattering can be read in (CCOM option 1) or calculated from the intensity at the highest angle. It is assumed that the intensity at this highest angle is the sum of incoherent and coherent scattering of individual atoms (no crystalline diffraction). The program will then calculate the sum of the coherent and incoherent intensities for the sample's composition from literature values [11c, 11d, & 12], which are present as internal look-up tables. The scattering factors are tabulated, as in the original references, as values at equally spaced $\sin\theta/\lambda$. The value at the angle of interest is calculated internally by an interpolation loop.

Both coherent and incoherent scattering factors are calculated to get the incoherent scattering intensity as a fraction of the total intensity at the highest angle by assuming that there is no diffraction intensity at that angle:

$$I_{tot} = I_{inc} + |f|^2_{coh} \qquad (11)$$

where I_{tot} is the total scattering intensity,
I_{inc} is the sum of the incoherent intensities, and
$|f|^2_{coh}$ is the mean-square coherent atomic-scattering factor.

The coherent and incoherent intensities are calculated from the sample composition and the individual atom's tabulated values using Equations 12 to 14.

$$|f|^2_{coh} = \{\sum_i N_i f_i^2\} / \sum_i N_i \qquad (12)$$

where f_i is atomic-scattering factor for the i-th type atom, and
N_i is the number of i-th atoms in the stoichiometric formula.

$$I_{inc} = R \{\sum_i N_i I_{inc_i}/R\} / \sum_i N_i \quad (13)$$

where R is the recoil factor for the scattering angle and wavelength,

I_{inc_i}/R is the tabulated incoherent intensities divided by the recoil factor for the i-th atom.

$$R = (1+ \frac{2h\lambda}{mc} \sin^2)^{-3} \quad (14)$$

where h is Planck's constant,

m is the rest mass of an electron, and

c is the velocity of light in vacuum.

The ratio of the calculated total scattering intensity at the maximum angle to the calculated incoherent intensity is then used to scale the calculated incoherent intensity at all the other angles. The incoherent intensity can be entered in the data file using CCOM rather than being calculated at the maximum angle but the rest of the procedure is the same. The calculated and scaled incoherent intensity is then subtracted from the total intensity at all angles.

The energy of the incoherent scattering is slightly less than the energy of the coherent scattering because it is due to inelastic interaction. This is why the recoil energy term is required for the incoherent intensity, which is dependent on both the incident energy and the scattering angle.

2.2 DEGREE OF CRYSTALLINITY

The degree of crystallinity of a sample is of particular interest in semicrystalline polymer systems. In theory the measurement of the crystallinity is simply the ratio of the crystalline contribution to the total of any material property. For x-rays this property is the diffracted intensity:

$$X_{cr} = \frac{I_{cr}}{I_{tot}} \tag{15}$$

In practice the determination of the crystalline contribution is quite difficult if precise absolute values are needed. Ruland describes [5] a method for separating the non-crystalline contributions to the total intensity and calculating a measure of crystalline disorder (see section 2.2.1). The extensive calculations and amount of experimental measurements make this method difficult to use. A simplified version of Ruland's method, easily applied with a computer, was published by Vonk [6] (see section 2.2.2). This program allows the user to choose either or both of these methods in the degree of crystallinity option (see section 3.2.4)

2.2.1 Ruland's Method

In high polymers the x-ray diffraction peaks are generally broader and more diffuse than other crystalline systems. The few crystalline peaks present also tend to overlap each other as well as non-crystalline scattering regions. Ruland's theory [5] accounts for the crystalline diffraction and the loss of intensity due to disorder in the crystals, such as thermal disorder and paracrystallinity [13].

Ruland defines the weight fraction crystallinity as:

$$X_{cr} = \frac{\int_o^\infty s^2 I_{cr}\, ds}{\int_o^\infty s^2 I\, ds} \cdot \frac{\int_o^\infty s^2 |f|^2\, ds}{\int_o^\infty s^2 |f|^2 D\, ds} \qquad (16)$$

where I_{cr} is the crystalline coherent intensity
I is the total coherent intensity,
$|f|$ is the mean square scattering factor,
D is Ruland's disorder parameter,
$s^2 ds$ is defined as the volume element of integration in s-space but can also be understood as the Lorentz correction.

The disorder parameter, D, is assumed to have the form $\exp(-ks^2)$ which includes thermal fluctuations and assumes the other lattice imperfections are generally isotropic.

A further assumption is that finite integration limits (s_o and s_p) exist such that:

$$\int_{s_o}^{s_p} s^2 I(s)\, ds = \int_{s_o}^{s_p} s^2 |f|^2\, ds \qquad (17)$$

is independent of the sample crystallinity and:

$$\int_{s_o}^{s_p} s^2 I_{cr}(s)\, ds = X_{cr} \int_{s_o}^{s_p} s^2 |f|^2 D\, ds \qquad (18)$$

Using the assumptions in Equations 17 and 18, Equation 16 may be rewritten as:

$$X_{cr} = \frac{\int_{s_o}^{s_p} s^2 I_{cr}\, ds}{\int_{s_o}^{s_p} s^2 I\, ds} \cdot K(s_o, s_p, D, |f|) \qquad (19)$$

where X_{cr} is a constant and

$$K = \frac{\int_{s_o}^{s_p} s^2 |f|^2\, ds}{\int_{s_o}^{s_p} s^2 |f|^2 D\, ds} \qquad (20)$$

The integration limits, s_o and s_p are determined experimentally, preferably with a common s_o. One then solves the equation by determining the series of K's that yield a constant X_{cr}.

An important intensity correction for this analysis is the subtraction of incoherent (or Compton's) scattering (see section 2.1.7). This correction requires a detailed knowledge of the chemical composition of the sample.

2.2.2 Vonk's Variation

Vonk [6] took the basic equations of Ruland's theory and defined the ratio, $R(s_p^2)$:

$$R(s_p^2) \sim K/X_{cr} \qquad (21)$$

where

$$R(s_p^2) = \frac{\int_{s_o}^{s_p} s^2 I \, ds}{\int_{s_o}^{s_p} s^2 I_{cr} \, ds} \qquad (22)$$

and K is defined by Equation 20. The symbol, ~, indicates that the left hand function oscillates about the right hand function.

When D has the form:

$$D = \exp(-ks^2) \qquad (23)$$

then K can be approximated by the first two terms of the exponential series:

$$K = 1 + b\, s^2 \qquad (24)$$

where b is a constant equal to k/2. Combining Equations 24 and 21, a plot of $R(s_p^2)$ versus s_p^2 should oscillate about a straight line defined by:

$$y = 1/X_{cr} + (k/2\, X_{cr})\, s_p^2 \qquad (25)$$

In the program the user inputs the integration limits and the crystallinity is calculated from such a plot. The plot can be viewed to determine if those integration limits do in fact give an approximate straight line.

A diffraction scan of the amorphous phase of the material is needed to use this option since precise separation of the crystalline and amorphous contribution is necessary.

2.3 CURVE FITTING

Curve fitting of diffraction data is used to separate the crystalline and amorphous contributions or separate overlapping peaks whose shape or breadth is of interest. This part of the program is very useful for examining diffraction patterns of new or unusual systems.

2.3.1 Available Options

There are a series of questions in the Fitting Option section (3.2.5) which define which of several fitting options the user wishes to use. This section will explain those options and rationales for choosing between them.

The first set of options are the same as the plotting options. The most useful fitting option is the I versus s; the curves can then be displayed or converted to either of the other options. The I x s^2 versus s fitting corresponds to the intensity plots in Ruland's degree of crystallinity determination or Vonk's variation of that technique but the program will convert the curves to this type from fits of either of the other options. I versus two-theta is a commonly displayed plot and again the program can convert the curves if another fitting option is used.

The options for the functional form of the fitted curves actually consist of the following three related distributions [14].

Pearson Type VII $$y(x) = y_o \, [1+(x-\bar{x})^2/(ma^2)]^{-m} \quad (26)$$

Gaussian $$y(x) = y_o \exp[-(x-\bar{x})^2/a^2] \quad (27)$$

Cauchy $$y(x) = y_o \, [1+(x-\bar{x})^2/a^2]^{-1} \quad (28)$$

where y_o is the peak intensity maximum,
$\bar{x}$ is center of the distribution,
m is the Pearson Type VII exponent,

a is related to the peak width according to the following relations:

Pearson Type VII	$\beta = 2a\ [m(2^{1/m} - 1)]^{1/2}$	(29)
Gaussian	$\beta = 2a\ [\ln(2)]^{1/2}$	(30)
Cauchy	$\beta = 2a$	(31)

where β is the full width at half the maximum intensity.

When the exponent, m, is 1 then the Pearson Type VII distribution reduces to the Cauchy, while as m approaches infinity the Pearson distribution approaches the Gaussian form. The shape of the distribution curves are very similar near the center but the Cauchy distribution has much higher y-values in the tail regions than a Gaussian distribution, which also increase the total area of the profile for any given y_o, and full width at half maximum. This can be seen in a plot of Cauchy and Gaussian curves, see Figure 3.

The program allows the user to fit curves to any one of these distributions. Since pure Gaussian or Cauchy forms are rarely seen except in special cases, those options are not used very much. Typically a mixture of Gaussian and Cauchy or the Pearson Type VII function is used. The choice between these two is dependent on the user preference. Mixed Gaussian and Cauchy curves can be used to obtain a fraction of each form since theoretically the Gaussian nature results from thermal fluctuations and the Cauchy nature from the incident beam spread. For most system such separation is not so clear cut and the decision on the option reduces to the one which by trial and error gives the least deviation from the experimental curve.

The weighting function is a means of giving certain intensity values different emphasis during the fitting. The exact place this occurs is explained in section 2.3.2. The weight functions available are the normallized square root of the intensity, this value being the standard deviation in intensity under constant counting time conditions; the reciprocal of the intensity, allowing better fits of the tail

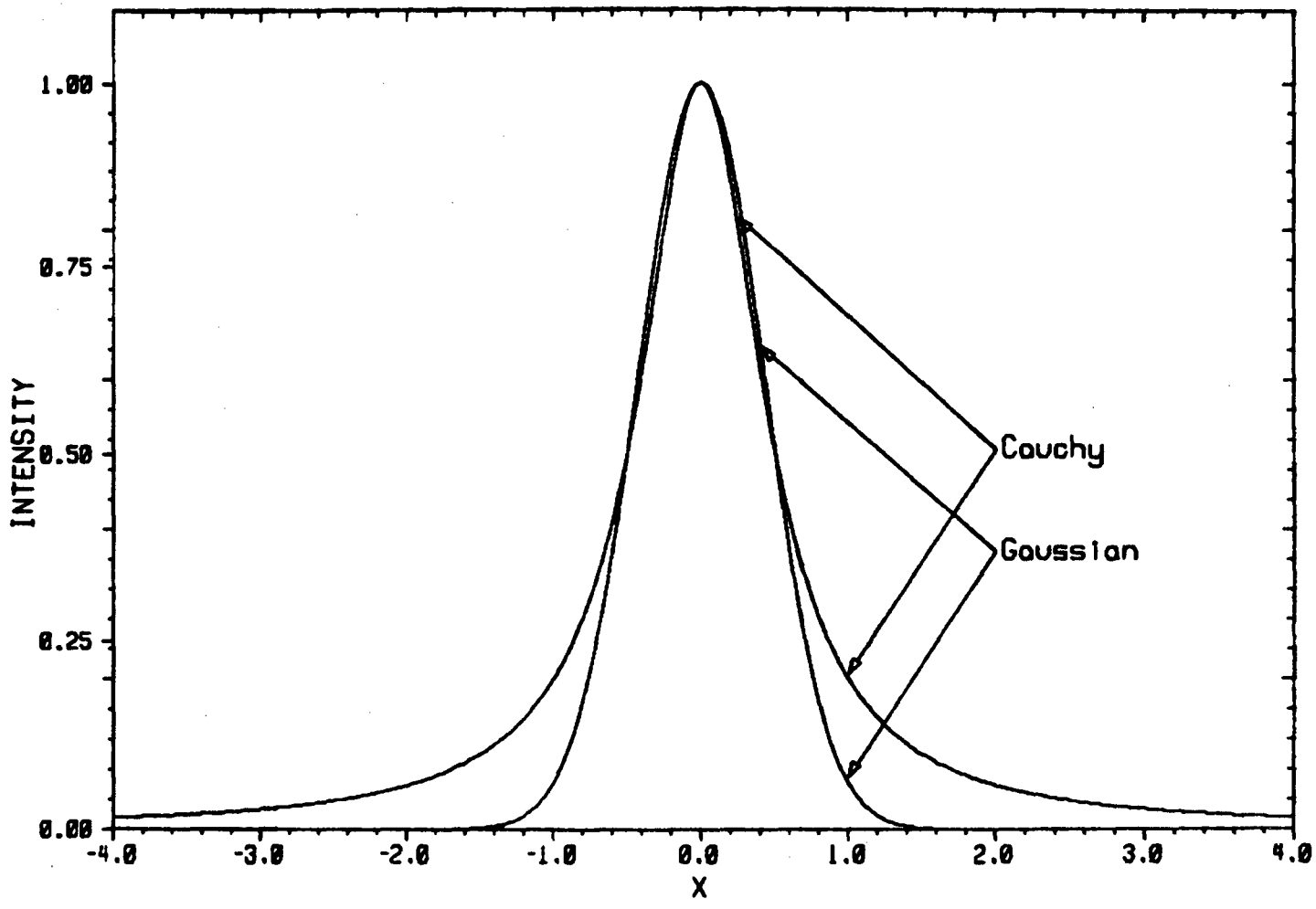


Figure 3. Comparison between Cauchy (m=1) and Gaussian (m=∞) profiles.

sections of the curves; and unity or no differences in weighting, used when constant counting statistics are used in the data collection.

The operator has the option of fitting one or two experimental scans if they exists. If you have an amorphous scan it should be used to eliminate errors arising from trying to fit that region of the diffraction pattern to a particular mathematical function. Diffraction from a second phase (such as fibers in a composite) can also be fit. A second phase can also be stripped out of the sample pattern by using the second phase stripping option (see sections 2.5 and 3.2.7).

The fitting parameters for the second scan(s) consist of the intensity mean value, its standard deviation, and the intensity at the mean position (the approximate maximum intensity is the only parameter the operator need enter). The program then calculates the partial derivatives based on the scan's data in terms of the position relative to the mean, in units of standard deviation, and scaled according to the intensity at the mean position.

Sometimes when fitting data with large scatter or peaks with shoulders, the program will not fit weak regions but instead set the corresponding input peaks to much different positions or sizes than they obviously should be. In these cases it is better to fit the large, strong peaks first and then fit the weak regions with the strong peaks' parameters fixed to the "best" fit from the initial fitting.

2.3.2 Gauss-Newton Method of Non-linear Least Squares

This method consists of defining an error function, SE, which is the sum of the squares between the experimental points and the fitted curve:

$$SE = \sum_i W_i \, (F_i' - Y_i)^2 \qquad (32)$$

where W_i is the weight given to the i-th point,

F_i' is the fitted intensity at i, and

Y_i is the experimental intensity at i.

The form of the fitted intensity, F_i', is taken from the functional form from the fitting options which define the several parameters to be varied by the program. This form is then expanded in a Taylor series with respect to all of those parameters (as many as 56) about the last approximate fitted intensity, F_i, for each point:

$$F_i' = F_i + \sum_j \frac{\partial F_i}{\partial p_j}\bigg|_{\tilde{p}_j} p_j \tag{33}$$

where $\tilde{p}_j$ are the estimated parameters defining the peaks being fitted and

p_j are the "corrected" parameters:

$$p_j = \tilde{p}_j + \Delta p_j \tag{34}$$

If we then define T_{ij}:

$$T_{ij} = \frac{\partial F_i}{\partial p_j}\bigg|_{\tilde{p}_j} \tag{35}$$

then SE may be rewritten as:

$$SE = \sum_i W_i \left(F_i + \sum_j T_{ij}\, p_j - Y_i\right)^2 \tag{36}$$

Taking all the derivatives of SE with respect to corrected fitting parameters and setting them equal to zero will yield a series of equations which when solved will give the minimum value of SE, or the least error. This is only true if the initial parameters are close to the correct ones since a drift towards a maximum is possible if one starts too far away from the correct values.

$$\frac{\partial SE}{\partial p_k} = \emptyset = \sum_i W_i (F_i - Y_i + \sum_j T_{ij} \Delta p_j) T_{ik} \quad (37)$$

or

$$\sum_j \Delta p_j \sum_i W_i T_{ij} T_{ik} = \sum_i W_i T_{ik} (F_i - Y_i) \quad (38)$$

Since both of these equations are repeated for all the parameters, p_k, they can be represented more conveniently in matrix form:

$$[B] x (\Delta P) = (G) \quad (39)$$

where $B_{jk} = \sum_i W_i T_{ij} T_{ik}$

$$G_k = \sum_i W_i T_{ik} (F_i - Y_i).$$

Solution of Equation 34 by diagonalizing the matrix, [B], gives values of Δp_j which can be added to the estimated $\tilde{p}_j$'s to give corrected p_j's. In principle this procedure need be performed only once but in practice many iterations are required to give the best fit.

The program asks for the initial fitting parameters and at the end of each iteration generates a new set of fitting parameters which should be better than the set used at the beginning of that iteration. The next iteration uses those new parameters as the approximate values and starts the entire process over again. The program will continue until the error values for each iteration converge on a single value or 30 iterations have been completed.

2.4 LINE BREADTH

2.4.1 Integral Line Breadth

The integral breadth option simply calculates the total integrated intensity in an angular range chosen and divides this value by the maximum intensity. The integral breadths calculated with this option can be used to calculate the size of crystallites by using the Scherrer equation [15]:

$$\beta = \frac{\int I \, d\theta}{I_o} \tag{40}$$

$$L = \frac{K\lambda}{2\,\beta\,\cos\theta} \tag{41}$$

Within this option there are three background correction alternatives. The first is no background subtraction at all, the second is a constant value for the background, and finally a straight line background connecting the intensities at the angular range limits.

The last method is preferred unless one or both sides of the peak profile are not separated from other peaks. This would necessitate one of the first two alternatives as well as careful selection of the range limits. The first alternative of no background should be used only when the background is very low or known to be less than the tail regions being examined.

2.4.2 Wilson's Variance Method

The Wilson's variance method of determining crystallite sizes stems from the difficulty of separating instrumental line broadening (β_i) from the total diffracted line profile (β_o). For Cauchy type profiles the line breadths or line widths are additive, while for Gaussian profiles the squares of the line breadths or widths are additive:

$$\beta_o = \beta_s + \beta_i \qquad \text{Cauchy} \qquad (42)$$

$$\beta_o^2 = \beta_s^2 + \beta_i^2 \qquad \text{Gaussian} \qquad (43)$$

These formulae derive from the fact that the observed profile {h(x)} is a convolution of the sample profile {f(x)} and instrumental factors {g(x)}:

$$h(x) = \int f(y)\, g(x-y)\, dy \qquad (44)$$

Pitts and Willets [16] and Wilson [4] noted that the variances of convoluted profiles are additive regardless of the profile shape. Wilson also showed that the variance changes with the range of angles examined and the background intensity subtracted from the total intensity. When the background is properly subtracted, the variance versus range plot produces a linear region at higher angular range values:

$$W = W_o + k\sigma \qquad (45)$$

where W is the measured variance,
W_o is the intercept of the linear region,
k is the slope of the linear region, and
σ is the angular range of the calculations.

The instrumental profile contribution to these variance parameters additive such that:

$$W_s = W_b - W_i \qquad (46)$$

$$k_s = k_b - k_i \qquad (47)$$

where s indicates specimen,
b indicates broadened observed values, and
i indicates instrumental values.

Two values of the specimen crystallite sizes (p) can then be calculated from these parameters:

$$p_W = \frac{L}{2\pi \ (-W_{os})^{1/2} \cos\theta} = \frac{1}{2\pi \ (-W_{os})^{1/2} \cos\theta} \tag{48}$$

$$p_k = \frac{K}{\pi^2 \ k_s \cos\theta} = \frac{1}{\pi^2 \ k_s \cos\theta} \tag{49}$$

where L is the taper parameter (related to the shape of the crystals) and

K is analogous to the Scherrer constant, both assumed close to unity.

Remember the program will calculate the slope and intercept in units of degrees 2θ, which must be converted to radians before inserting into the above equations.

In the program (adapted from a batch card deck [17]), the user specifies an initial range and the program uses the method of Pike and Wilson [18] to calculate the centroid position. The intensities in that range are splined into a 201 point equally spaced array with a straight line background of 90% of the range limit intensities.

$$\theta_g = \theta_z - \{\frac{\Sigma S}{T} + \frac{r}{1-r} [\frac{\Sigma S}{T} - \frac{n}{2} + \frac{(n+2)\delta}{12\ b}]\} \ \Delta\theta \tag{50}$$

where θ_g is the centroid location,

θ_z is the range upper limit,

ΣS is the partial sums of intensity:

$\Sigma S = I_1 + (I_1 + I_2) + (I_1 + I_2 + I_3) + \ldots,$

T is total observed intensity,

n is the number of steps, ie 200,

δ is the rise in background between the limits,

b is the average background in the range,

r is the ratio of total background to total observed intensity, and

$\Delta\theta$ is the angular range step.

A new range, symmetric about the centroid, is set and the variances, W, are calculated according to Langford and Wilson [19]:

$$W = \{\frac{\psi}{T} + \frac{r}{1-r}\,[\frac{\psi}{T} - \frac{n(2n+1)}{6} + \frac{n(n+2)\,\delta}{12\,b}]\}\ (\Delta\theta)^2$$

$$- \{\frac{\Sigma S}{T} + \frac{r}{1-r}\,[\frac{\Sigma S}{T} - \frac{n}{2} + \frac{(n+2)\delta}{12\,b}]\}^2\ (\Delta\theta)^2 \qquad (51)$$

where ψ = [I (n-i+1)] by definition,

n is the number of range steps (varied in this phase), and the remaining variables are the same as in Equation 50.

You will note that the second half of this equation is identical to the square of the second part of the centroid equation. The above equation is valid only when the variance range is centered near the centroid, which is why this position was first calculated.

In this section W is calculated as a function of range by varying n and a family of curves is generated by varying the background, b. The latter is important since the tail region is very much affected by the background chosen. The operator must decide from the plot of this family of variance-range curves which background gives the "best" linear region. Figure K-1 shows such a family of curves with the best linear region occurring with a background of 33.67.

A new background range may be examined to get better linearity, but once a suitable value is chosen the slope and intercept for that variance-range curve will yield the k_b and $W_o b$ for that sample and reflection. Subtraction of the instrumental slope and intercept will give two measures of the crystallite size. Differences in the two measures are a result of the assumption of unity for K and L.

This method is useful only when the peak being examined is fully separated from any neighboring diffraction peaks. Diffraction profiles which where broadened from instrumental factors only is required, i.e. very large crystals relative to the sizes of interest, such as produced by pressing pellets of recrystallized hexamethylene tetramine.

2.5 SECOND PHASE INTENSITY STRIPPING

This option allows the user to subtract the intensity from one phase from the sample scan. This is most useful with materials that contain several diffracting species, one of which interferes with the scan of interest. A scan of the phase one wishes to delete from the sample scan is needed as well as a knowledge of where the scans intensity's fall to a baseline

The program draws a baseline at the two angles input on both the sample scan and the second phase scan. It then scales the maximum intensity of the second phase to the same angular position on the sample scan and subtracts that intensity from the sample scan.

$$I_c = I_1 + \text{constant} \times I_2 \qquad (52)$$

The program having the composite scan (I_c) and second phase scan (I_2) uses the relative intensities of the phase of interest (I_1) to calculate a scaling constant. The scaled second phase is then subtracted from the composite scan so that the user can use any of the other analysis options on the stripped sample scan.

SECTION 3

OPERATION OF PROGRAM

3.1 DATA FILE

Preliminary instructions must be inserted at the beginning of the data file preceding the diffraction data. The actual collection of diffraction data and entry onto the computer is dependent on the instrument used and that procedure is described elsewhere [7] and [8].

Appendix A lists part of a data file for data taken on the Picker FACS-1 diffractometer, including preliminary instructions in the Predata section.

3.1.1 Predata Section

Preliminary instructions are put onto the data files as four letter codes at the start of each line at the beginning of the file. These code groups are explained below, including some that require numbers on the same line. The code "END" is placed at the end of all Predata sections. A Predata section, changing plotting, printing or compositional information may precede any data set by begining the new section with the code "PRED". The program will ignore one or two lines in a Predata section which do not correspond to correct codes, but a third incorrect line will terminate the program.

The order in which each of these instructions occurs is unimportant so long as all the desired codes are placed before the END code. In the explanations below an I following a code group indicates an integer follows the code while an R indicates that a real number follows the code. If these numbers are in quotes (e.g. "R") then that number is optional and may not be needed.

These code words and the pages on which their expanation is given are summarized alphabetically in Table 1 for quick reference.

TABLE 1. Alphabetical Listing of Predata Code Words

Code Word	Page	Use after PRED
ABSB R "R" "R"	29	No
ABSL R "R" "R"	29	No
AMOR I	30	Yes
AXIS I,I,I	29	Yes
BACK	30	Yes
CCOM I "R"	30	No
COLO	29	Yes
END	26	Required
FIBR R R	29	Yes
FILM R R	29	Yes
HEAD string	28	Yes
INTR	28	No
KILL R	28	Yes
LENG R	29	Yes
LEVP I	28	No
NOPL	28	No
NBRO R	31	Yes
NCAR R	31	Yes
NCHL R	31	Yes
NFLO R	31	Yes
NHYD R	31	Yes
NNIT R	31	Yes
NOXY R	31	Yes
NPHO R	31	Yes
NSUL R	31	Yes
PAIR	28	No
PHOT	28	No
PICK	28	No
POLM R	30	Yes
PRED	26	Required
SECD I	30	Yes
WAVL R	31	Yes
ZERO	29	Yes

Predata instructions for the operation of the program are explained below:

HEAD followed by the title of the data file on the same line will cause the program to read that title and print it at the appropriate places until another title replaces it.

INTR tells the computer that the program will be run interactively (default is non-interactive).

The source of the data is indicated by one of the next three codes:

PICK indicates the data was collected on the Picker FACS-1 (default data format).

PHOT indicates the data was output by the PHOTO analysis program and should be as x-y pairs of Bragg angle and relative intensity or optical density. Optical density conversion to relative intensity is an option in this program.

PAIR indicates the data consists of x-y pairs of Bragg angle and intensity obtained from any source. The first line of each set should contain the data set title, and the last line must be a pair of 999s.

LEVP I is the print option request:

I = Ø - no data is printed (default),

I = 1 - all corrected data to be written on file DIFF.INT,

I = 2 - all fitted data and parameters to be printed on files FIT.DAT and FIT.PAR respectively,

I = 3 - both print options 1 and 2.

NOPL suppresses all plots.

KILL R tells the program to set all intensities below "R" Bragg angle to zero, essentially ignoring that region.

COLO turns on the color option for off-line Calcomp plots or AED terminal plots.

LENG R for remote non-interactive plotting, sets the x-axis length to "R" inches. R must be between 2 and 36 or the default value of 9 will be used.

ZERO will cause a line to be drawn through zero intensity if negative intensities are present during remote non-interactive plotting.

AXIS I,I,I sets the axis options for remote non-interactive plotting (1,Ø,Ø is default):

I = Ø - Do not plot this option,

I = 1 - Plot this option.

Axis options are any of these:

1st # - Intensity versus two-theta,

2nd # - Intensity versus s, where s=1/d,

3rd # - s^2 x Intensity versus s.

The next set of code groups informs the program of the intensity corrections to be carried out. The first four codes are different absorption options of which only one of the four may be used.

FIBR R R (Fiber samples only) the first number is the sample density, and the second number is the fiber radius.

ABSB R "R" "R", etc. (Fiber samples only) each number up to 2Ø values is a μR for the respective data set.

FILM R R (Film samples only) the first number is the sample density, and the second number is the thickness in centimeters.

ABSL R "R" "R", etc. (Film samples only) each number up to 2Ø values is a μt for the respective data set. Normal transmission geometry is assumed for PHOTO data and symmetric transmission (theta -

two theta) assumed for the other film absorption cases. If an omega angle is specified, this angle is used to calculate the deviation from symmetric transmission and the corresponding absorption.

CCOM I "R" defines how the incoherent scattering will be corrected:

I = Ø - no incoherent scattering corrections (default).

I = 1 - the incoherent scattering factor at the maximum angle is read in (R) for use on all data sets.

I = 2 - the incoherent scattering factor is calculated for all the data sets using the intensity at the maximum angle of the first data set.

I = 3 - the incoherent scattering factor is calculated for each data set using the intensity at the maximum angle of each data set.

Other correction information uses the following codes:

BACK indicates the background or air scattering scan for the diffraction data follows the next sample data scan. This was set up so that the background can be changed for different samples on the same data file and typically a background scan is collected after the first successful data scan to use with the rest of the data scans.

AMOR I indicates an amorphous scan is data set I.

SECD I indicates a second phase is data set I (may be the same as AMOR).

POLM R sets the polarization constant for a crystal monochromator whose diffraction plane is perpendicular to the sample diffraction plane such as in the Picker case.

R = 1.ØØØØ - for no monochromator (default),

R = Ø.7986 - for Copper radiation monochromator,

R = Ø.9553 - for Molybdenum radiation monochromator.

WAVL R sets the wavelength of radiation to "R". If none is given the default wavelength is 1.5418 Å of copper Kα.

The sample composition is sometimes needed for analysis as mentioned above. If the composition is not given in this Predata section as explained below and the program is in interactive mode it will request the composition. If no composition is entered anywhere and an option requested needs the composition then the option is dropped by the program and reverts to the default position.

The composition is read in as follows: the four letter code for each of the elements below starts a line followed by the number of atoms of the element in the molecular formula. Mixtures may be input as weighted average formulas. Any element not listed is assumed not to be present and only those listed below may be used.

NHYD R = number of Hydrogen atoms,
NCAR R = " " Carbon " ,
NNIT R = " " Nitrogen " ,
NOXY R = " " Oxygen " ,
NFLO R = " " Fluorine " ,
NCHL R = " " Chlorine " ,
NSUL R = " " Sulfur " ,
NBRO R = " " Bromine " ,
NPHO R = " " Phosphorus " .

3.1.2 Data Stacking

The actual intensities must immediately follow the predata information on the data file. If the data was obtained from the Picker FACS-1, the entire teletype output can be used as the data sets. For PHOTO the information on the "SAVE" file can likewise be used directly. Data pairs can have only a single line of "heading" characters followed by the Bragg angle-intensity pairs.

The intensity data sets must follow the sequence laid out in the Predata section. If μt values were input then the order of the data sets must correspond to the respective μt values. For this purpose, background scans are not counted as data sets.

Plotting, printing, or compositional information may be placed between data sets by inserting the proper Predata codes between "PRED" and "END" code lines (see Table 1 for the allowable codes following "PRED").

3.2 OPERATIONAL SEQUENCE

The operational sequence given in this section describes the operation of this program in the interactive mode. If the program is to be run non-interactively, the data file filename must be entered in the sequence of commands so that the program can open that file and the plot file, "DIFF.PLT", must be spooled after the run is complete. Non-interactive operation only allows intensity corrections and off-line plotting of the data with any printing or plotting instructions embedded in the Predata sections of the data file.

3.2.1 Preliminary Data Entries

An example of the initial output from running this program is shown in Appendix B (underlined letters and numbers are user input in all appendices). The first information requested by the program is the name of the data file. The program will open this file so that the data can be read into the program for corrections and analysis. The program reads the Predata section and lists those instructions and information so that the operator can decide if any changes should be made.

The second question asked is to input the type of terminal from which you are operating the program. This will set internal flags for the proper plotting commands etc. This program was originally written for use on a Tektronix terminal. If a non-plotting terminal is used then the program will not erase the screen at the places indicated below.

After erasing the screen the file heading will be written followed by the sample set heading, date, time, and intensity correction information. If an amorphous scan or second phase scan is present, the program will print an informational line showing that the the scan's smoothed intensities have been assigned to the appropriate internal arrays for further use.

When print option 1 or 3 (see LEVP in the Predata section) is called the positions, corrections, and intensities are written on DIFF.INT while the corrections are being calculated. An example of this output is given in Appendix C.

When the intensity corrections are complete the program will automatically request a decision on plotting.

```
DO YOU WANT TO PLOT THIS DATA SET?  Y/N
```

If you answer "yes" then the program will go to the Plotting section (see 3.2.3 below). If you answer "no" (default) then the program will go to the Option section (see next section). Here and elsewhere in the program the letters, Y, will suffice for a "yes" response and an N will suffice for a "no" response.

3.2.2 Option Section

Whenever the user goes into the Option section of the program, the following will be printed:

```
OPTIONS ARE:

     1=CONTINUE TO NEXT DATA SET
     2=GO TO PLOTTING SECTION
     3=WEIGHT FRACTION CRYSTALLINITY CALCULATIONS
     4=CURVE FITTING CALCULATIONS
     5=LINE BROADENING CALCULATIONS
     6=SECOND PHASE STRIPPING
     7=EXIT PROGRAM

ENTER OPTION NUMBER
```

If any number other than 1 to 7 is entered, then an error message followed by the same option listing will be printed. Options 2 through 6 are explained in sections 3.2.3 through 3.2.7 respectively. The

screen will erase before proceeding to the desired option.

Option 1 will read in the next data set, replacing the current data set with the new. This new data set will then be corrected as the previous set with the same output sequence given in section 3.2.1, beginning with the writing of the data set heading, time, date, and intensity correction information.

Option 7 will terminate the program. A message that the program is finishing will be printed while the program automatically closes all files.

3.2.3 Plotting

Appendix D has all the necessary questions and answers for plotting and several plots. When you enter the Plotting section, either by answering "Y" to the plot question after the intensity corrections or by going to Option 2, you will be asked:

```
WHAT DO YOU WANT TO PLOT?  TYPE APPROPRIATE NUMBER
     1=INTENSITY VERSUS TWO THETA
     2=INTENSITY VERSUS S, WHERE S=1/d
     3=(S**2)*INTENSITY VERSUS S
```

The first two plot options will produce plots of intensities with all corrections applied except the Lorentz correction, which tends to blow-up at high angles (see section 2.1.2). The choice between options 1 and 2 is a choice between abscissa axes of diffraction angle or the reciprocal of the lattice spacings (s). The s^2 x Intensity ordinate option (3) is the Lorentz corrected intensity for random powders and bulk crystallized polymers. This type of plot is used for the degree of crystallinity measurements, q.v.

The diffraction curves as plotted in any of these three ways can be curve fit in Option 4; it is therefore useful to preview the particular curve as a plot before fitting so that the approximate fitting

parameters can be estimated.

The program will then ask:

```
DO YOU WISH TO CHANGE THE X OR Y AXIS LENGTH?  Y/N
DO YOU WANT THE COMPUTER TO CHOOSE THE AXIS SCALE?  Y/N
```

The default answers to both questions is no. The default axis lengths are 9 inches in X and 6 inches in Y, which fits nicely on terminal screens and standard size paper. You can have the computer determine the axis scales by answering yes to the second question but the algorithm may not scale similar plots the same, making comparisions difficult.

When the program user is inputting the axes scales, the following information and questions are printed:

```
XMIN=  00.0000 XMAX=  00.0000 XDELTA=  00.0000
TYPE IN XMIN AND XMAX ON THE SAME LINE...
```

The desired range can then be input, either covering the entire range or any part of it. The XDELTA value is simply the range divided by the axis length.

When the starting and ending values are entered, the program will list these new XMIN and XMAX values and ask if they are satisfactory.

```
XMIN=  00.0000 XMAX=  00.0000 XDELTA=  00.0000
DO YOU WISH TO CHANGE THESE?  Y/N
```

If you answer yes then the program will again request new XMIN and XMAX values and continue this loop until you are satisfied. When you are satisfied, answer no to the question (default answer), and the program will go through the same process for the Y axis. When a user is experienced this process does not take much time and is more reliable then letting the program chose the scales.

The above part of the Plotting section also describes plotting parts of some of the other sections and in fact calls the same internal subroutines.

How you want the intensity data displayed is posed in the next question:

```
HOW DO YOU WANT THE DATA DISPLAYED?  TYPE N
     N<Ø DRAWS A SYMBOL AT EVERY NTH POINT
     N=Ø CONNECTS ALL POINTS WITH A STRAIGHT LINE
     N>Ø DRAWS A SYMBOL AT EVERY NTH POINT AND CONNECTS WITH A LINE
```

You must enter an integer which tells the program how you want the data displayed and how much of the data you want displayed. The symbol for the data points has been set internally to be a triangle.

The next question involves grids on the plot:

```
DO YOU WISH TO DRAW LINES ON YOUR PLOT?  Y/N
TYPE IN THE LINE SPACING IN INCHES FOR X AND Y AXES, ON THE SAME LINE
```

If you answer no to the first question (default) then the second one will not be asked. The grid you choose can be square or rectangular simply by entering the line spacings.

Only if the intensity range chosen includes negative values will the next question be asked:

```
DO YOU WANT A LINE AT ZERO Y-AXIS VALUE?  Y/N
```

Negative intensities may occur when some of the corrections are greater than the raw intensity because the corrections are in error, or the more likely event, the scatter in the raw intensities is large.

The program then asks if you want to start the plot. A yes (default) will then cause the plot to be generated at the screen or

off-line if you are not at a plotting terminal. If you are at a plotting terminal the program will wait until you hit carriage (CR) return before erasing the plot and asking if you also want a Calcomp plot. At a non-graphics terminal the Calcomp plot generation on file "DIFF.PLT" is the only plot generated.

START PLOT? Y/N

The curve will then be plotted according to the instructions entered. See figures D-1, D-2, and D-3.

CR
DO YOU WANT A CALCOMP PLOT? Y/N

A no answer to the start plot question will return the user to the beginning of the Plotting section. When the plot and Calcomp plot question are completed the program will return to the Option section.

3.2.4 Degree of Crystallinity

Examples of degree of crystallinity measurements using Option 3 is given in Appendices E and F. Both of these methods can be called by Option 3 and have some questions in common.

DO YOU WANT THE ORIGINAL RULAND ANALYSIS (Y),
OR THE VONK MODIFICATION (DEFAULT)

This first question deterimines which method will be used for the remainder of this option. If you want to try both methods on the same data set, you have to call Option 3 twice. An amorphous scan is required to use the Vonk method in Option 3, however if the data is curve fit, then the first fit curve is assumed to be the amorphous peak in the Vonk analysis part of that Option.

Both methods will ask how you want to enter the angular ranges, either by marking a plot with cursors or by entering the s-space values

of the ranges.

DOES YOUR TERMINAL HAVE CURSORS? Y/N
TYPE IN THE NUMBER OF REGIONS YOU WISH TO ANALYZE

These questions set up the number of regions and how you are to input the ranges. The maximum number of regions allowed is 1Ø. The range limit positions should be between crystalline peaks where most of the diffraction is due to the amorphous phase. The number regions will depend on the number of peaks, generally the number of regions being equal to the number of low spots in the diffraction curve. The s-space values entered will be one more than the number of regions with the initial value being at as low an s as possible in the scan.

YOU ARE IN THE CURSOR MODE.
*** PREPARE TO PLOT ***
TYPE IN THE VALUES FOR So----Sn YOU WISH TO USE

If you are at a terminal with cursors the first two lines will be printed, followed by axis scaling questions (see section 3.2.3). The cursors will come up on the plot so that you can mark positions you want as s_o and s_p. If you are re-entering this option and/or already know the s values you want, tell the program you are not at a terminal with cursors and type in the s values following the last line above.

The program finds the closest data point to the requested region limits and prints the corresponding s and Is^2 values.

POINT = # S = Ø.ØØØØØ Is**2 = Ø.ØØØØØ

You may preview these regions to see if they fall at the desired places and either continue or re-input the region data. As before, plotting will require scaling questions.

DO YOU WANT TO SEE A PLOT OF THE REGIONS YOU HAVE CHOSEN? Y/N

ARE YOU SATISFIED WITH THESE REGIONS? Y/N

If you want to try other regions answer no to the above question and you will return to the region limit input.

Once the regions have been set, the program will follow different paths for the two different methods. The Ruland method will calculate the ratio of crystalline to total intensity for a family of disorder parameters and print out these ratios as degrees of crystallinity and the K values for that region (see Equation 20). First enter the range of k values you wish to examine, 0 to 9 is a good starting point.

TYPE IN DISORDER PARAMETER (k) RANGE AND DELTAk
THE MAX # OF ks IS 10

DISORDER PARAMETER= 0.000

So - Sp	DEGREE OF CRYSTALLINITY	BIG K
0.0000 - 0.0000	0.500	1.0000

The coefficient of variation in the degree of crystallinity for each disorder parameter is listed next, then an average degree of crystallinity:

COEFFICIENT OF VARIATION (%)	0.000
MEAN WEIGHT FRACTION CRYSTALLINITY ?	0.000

You want to use the disorder parameter with the lowest variation in crystallinity. You can chose this disorder parameter from the listings or from a plot of the coefficient of variation versus disorder parameter:

DO YOU WANT TO SEE A PLOT OF VARIATION FACTOR VERSUS DISORDER PARAMETER k? Y/N

The option exists to examine another family of disorder parameters, either to narrow in on the best value, or to broaden the field examined. The operator also has the option of trying different regions and repeating the entire process before finishing this option.

DO YOU WANT TO CHOOSE A DIFFERENT DISORDER PARAMETER REGION? Y/N
DO YOU WISH TO TRY DIFFERENT VALUES FOR So----Sn? Y/N

*** WEIGHT FRACTION CRYSTALLINITY CALCULATIONS ARE FINISHED ***

When you ask to use the Vonk method, which is a variation on the Ruland method, the program also calculates the ratio of crystalline to total intensities for each region. In this case, however; the degree of crystallinity is calculated from the intercept of a plot of the intensity ratios versus the end of the respective region (see equation 21). The disorder parameter is also calculated here from the slope of that line.

A different summary is printed, but you can still obtain a plot showing what was done analytically by the program. You may decide from the plot whether the regions chosen gave a good straight line or not.

CRYSTALLINITY = Ø.5ØØ +/- Ø.ØØØ
DISORDER PARAMETER (k) = 2.ØØØ +/- Ø.Ø5Ø

So - Sp	R of TOT/CR	Sp **2
Ø.ØØØØØ - Ø.ØØØØØ	Ø.ØØØØØ	Ø.ØØØØØ

DO YOU WANT TO SEE A PLOT OF TOTAL TO CRYSTAL INTENSITY RATIO vs Sp**2

If desired the entire process can be repeated for a different set of regions. When the degree of crystallinity measurements are completed the program will return to the main program Option section.

DO YOU WISH TO TRY DIFFERENT VALUES FOR So----Sn? Y/N

*** WEIGHT FRACTION CRYSTALLINITY CALCULATIONS ARE FINISHED ***

Return to Option section (see section 3.2.2).

3.2.5 Curve Fitting

A complete example of curve fitting is shown in Appendix G. This section will describe the various questions and sequence of events depending on the options chosen.

If you plotted the data before you enter Option 4, the program will ask if you want to fit the entire data file or only the part plotted. Then the program will ask you if you want to fit your data. This is a check question which allows you to change your mind without entering all the fitting parameters.

As shown in Appendix G the next series of questions asks about the curves' form, fitting function types, and the weighting factor. Each question must be answered with a single integer in the range given in the question menu or an error message will be printed.

Next the x-axis range in which you want to fit is requested:

```
FROM WHAT INITIAL POSITION TO WHAT FINAL POSITION?
.12  .355
```

The program then finds and prints the nearest corresponding points and some normalization information.

```
THE MIN POS IS Ø.11869  THIS IS THE   2 DATA POINT
THE MAX POS IS Ø.35537  THIS IS THE 171 DATA POINT
THE TOTAL NUMBER OF DATA POINTS TO BE FITTED IS 17Ø

THE AVERAGE S IS    Ø.26Ø51 AND THE AVERAGE RCI IS   3.56546
```

You must then enter the number of background points which also fixes the baseline fitting polynomial order to one less than the number of baseline points (i.e. 2 points for a straight line baseline).

TYPE THE NUMBER OF BASELINE POINTS (2 TO 6)

TYPE THE APPROX. POSITION AND INTENSITY OF THE BASELINE
1 FIXES THE INTENSITY, Ø DOES NOT EG:
.123 Ø Ø.1234
.345 Ø 1.2345

You then enter the position and first approximation of the intensities at those positions. The baseline intensities should be low particularily if the total intensity curves drop near zero at the ends of your fitting range. The integer preceding the intensity must be a Ø or 1; the 1 fixes the intensity while the Ø allows the program to vary that intensity when it is trying to fit the total curve.

The fitting parameter input is free formatted so that exact spacing of numbers is not needed. The sequence of floating point numbers and integers in the examples must be adhered to, however; or the program will re-request the entire input block.

If an amorphous scan is present the program will ask if you want to use that scan or ignore it. If you intend to enter this amorphous scan into the fitting, then an approximate peak height is also needed; the initial position, breadth, and shape will be calculated from the scan itself.

DO YOU WANT TO FIT THE AMORPHOUS SCAN TO THIS DATA SET?
TYPE INITIAL AMORPHOUS PEAK HEIGHT FOR FITTING, EG:
2.123

If a second phase is present a similar set of questions will be asked for fitting that second phase.

The actual peak parameters are entered next. This is the position in the program where the user will find a plot of the data most useful. Approximate peak positions, peak intensities, and breadths must be estimated and put in as below. The number of peaks to be fitted does not include the the amorphous or second phase scan if you are fitting them, however; 12 is the maximum number of total peaks counting any amorphous or second phase scan as one peak.

```
TYPE THE NUMBER OF PEAKS TO BE FITTED (MAX OF 12)
  PEAK POS     INT AT MAX      FW-HM      EXPONENT
Ø .212  Ø 4.123  1 .ØØ6  Ø .5  FOR EXAMPLE
Ø .345  Ø 9.876  1 .ØØ12  Ø 4.Ø
```

If you are fitting to a mixed Gaussian/Cauchy profile then the Gaussian fraction initially input should be one-half except in specific cases where another value is known. The Pearson exponent should likewise be a median value; a value of 4 works fairly well.

When these parameters are input, the program erases the screen; prints the title, date and time, and weight function; and then lists the sum of errors (SE) for each fitting iteration. The actual parameters used in each iteration are not printed but are saved on the FIT.PAR file when print option 2 or 3 is used. The SE listed here is not identical to the one listed in the Theory section (2.3.2), but is normalized for the number of points, weighting, and absolute intensities. This allows you to compare the SE for any fit directly with the SE from any other fit

The exponent for SE was chosen from experience such that when its mantissa approaches unity then the fit can be considered good. It is not unusual for the initial SE to be several orders of magnitude higher than the final SE, even when the final parameters do not appear too much different from the initial ones. The value of SE will generally drop very fast in the first few iterations and then much more slowly. The SE may be seen to increase occasionally which is usually due to the Pearson exponent or Gaussian fraction being set outside the real range by the

program and then being reset within the real range. If the value of SE begins by increasing or oscillating greatly, then the input parameters were not close enough to the correct values and the program is searching for a saddle point and not the minimum SE.

There are two error messages possible during the curve fitting:

```
MATSOL-PIVOT IS ABOUT     1.12D-16 FOR RANK  7
MATSOL-PIVOT TOO SMALL    2.23D-36
```

The first message just indicates the "pivot" or divisor in the matrix inversion subroutine is very small, which may cause errors. The second message indicates the pivot is too small to be handled by the program, effectively causing a division by zero. The first message is a warning that indicates an error may eventually occur, but not necessarily. It is not unusual to see this warning one or two times during a fit with out any problems developing. The second is a fatal error which stops the curve fitting. The pivot becomes small when one parameter is so close to the correct value, relative to the others, that it has no change during that iteration. To overcome this error, refit the data using the parameters at the time of the error but rounded off or change the Pearson exponent (or Gaussian fraction). The latter is an option in the refit part of this section (see below).

When the program has calculated through enough iterations for the sum of errors to converge (or reached the maximum of 30 iterations), the final "best" fit parameters will be printed along with the most commonly used information calculated from the fitting parameters. This other information includes reflection d-spacing from the peak positions, area under each peak, and integral breadth of each peak.

Each fitting parameter is also preceded by an integer, either 1 or 0 to indicate whether that parameter was fixed or not. This is included not only to remind the user which parameters were fixed originally but also indicate which of the last parameters were fixed by the program. The program includes routines to prevent the Gaussian fraction from

being set outside Ø.Ø to 1.Ø or the Pearson exponent from being set below 1.Ø. If the program tries to do so three times, the check routines set that parameter to that limit and fix it there.

Limitations on the size of numbers (within the computer itself) necessitated a limit of 5ØØØ as a maximum for the Pearson exponent. When the exponent is listed as 5555, it means the program attempted to set that exponent above 5ØØØ three times so the parameter was fixed to give a Gaussian profile. The amorphous peak's Gaussian fraction or Pearson exponent is always set at a fixed -1.Ø but this is just a dummy parameter used to keep the number of parameters per peak constant. The second phase's dummy parameter is set to -2.Ø.

After the final fitting parameters are printed the program will ask several questions:

DO YOU WANT A PRINT-OUT OF THE FITTED DATA?
DO YOU WANT A PLOT OF THIS FIT?

No is the default answer to both questions, causing the program to continue to the next question. A Yes to the first question produces a print-out of all the individual peak intensities, total fitted intensity, and the experimental intensity at each point. This information is written on FIT.DAT with print options 2 or 3 (see Appendix I). The second question, when answered affirmatively, is followed by axis scaling questions (see section 3.2.3) and a plot. The experimental data is always plotted as triangles with solid lines being the fitted curves. The same plot options as Option 2 are available despite the fitted form of the curves. Any number of plots may be generated including off-line Calcomp plots.

DO YOU WANT TO STRIP THE SECOND PHASE FROM THIS DATA?

The second phase, when stripped here, stays stripped only so long as you do not return to the main program option mode. It is recommended that weighting option 1 (1/Y) be used if stripping is to be done to

decrease the possiblity of negative "stripped" intensities from being produced. The program will ask if you want the stripped curves plotted and then proceed with the rest of the available analyses in this option.

DO YOU WANT A VONK ANALYSIS OF THESE CURVES?

The Vonk analysis follows the same path as in the degree of crystallinity section (3.2.4) except a continuous ratio of total to crystalline intensity is plotted instead of breaking the diffraction curve up into sections.

At the end of plotting and the Vonk analysis a refit question is posed:

DO YOU WANT TO REFIT THE DATA?

DO YOU WANT TO START WITH THE LAST "BEST" FIT PARAMETERS?
(EXCEPT THE EXPONENTS WHICH WILL ALL BE SET TO 4.Ø) or
(EXCEPT THE GAUSS FRACTIONS WHICH WILL ALL BE SET TO Ø.5)

This refit option and questions will also be called if the maximum of 3Ø iterations is reached or the if the MATSOL-PIVOT is too small. A no to the first question terminates the fitting option without printing the second question. A yes to the second question will begin the refitting. A no will return the program to asking for the number of background points and other fitting parameters. If a different fitting region or curve form is desired, the user must respond no to the refit question and then ask for Option 4 again in the main program Option section.

3.2.6 Line Broadening

The line broadening measurements are called by asking for option 5 in the Option section. Which method you want to use is the subject of the first question:

DO YOU WANT SIMPLE INTEGRAL BREADTH (S), OR
WILSONS VARIANCE METHOD (DEFAULT)OF LINE BREADTH?

An answer of "S" will call the integral breadth subroutines as demonstrated in Appendix J. Any other response will call the Wilson's variance subroutines (see Appendix K).

The integral breadth path will then ask if you want a Baseline, which is a background correction. If you do, then the program will ask if you want a constant intensity correction. Having a baseline line correction is the default but the constant intensity correction is not. If you want a constant intensity correction you must also enter that value. The default alternatives of a non-constant baseline will cause the program to calculate the baseline from a straight line between the two-theta limits of the peak area.

DO YOU WANT A BASELINE? Y/N
DO YOU WANT CONSTANT INTENSITY CORRECTIONS? Y/N
TYPE IN INTENSITY CORRECTION
TYPE IN THMIN AND THMAX FOR PEAK AREA

The range you want to examine is the next input. Once this is entered, the program will calculate the integral line breadth in degrees two theta, print that answer and ask if you want to try another peak. Unless you want to go to another two-theta range the program will return to the Option section of the main program.

The Wilson's variance method will immediately ask for the peak range of interest:

ENTER INITIAL AND FINAL TWO-THETA RANGE FOR PEAK

The program will calculate a baseline of 90% of the intensity at the extreme edges of the range (typical final background) and use that background to calculate the centroid's position. The program then uses the new range to set a symmetric range about the centroid. The program

will use this range and ten background intensity levels from 10% to 100% of the range end intensities to calculate a family of variance-range curves. The desired straight line region of these curves is searched for by the computer and the background that produces the best straight line is listed as the one with the minimum error:

```
INITIAL AVERAGE BACKGROUND = 00.0000

THE CENTROID OF THE PEAK IS LOCATED AT :  00.000
   THE OLD LIMITS WERE :  00.000  TO  00.000
   THE NEW LIMITS ARE  :  00.000  TO  00.000

MINIMUM BACKGROUND IS  0.0000
                       (this message to remind the operator that this
 **  WAIT  **          phase takes time due the many operations being
                       performed by the program.)
MAXIMUM BACKGROUND IS 00.0000

MINIMUM ERROR OCCURS WITH A BACKGROUND OF 00.0000
   DO YOU WANT A PLOT OF THESE VARIANCES (Y) OR
   DO YOU WANT TO TRY OTHER BACKGROUNDS (N) ?
```

A plot of the variance-range curves can be very helpful in deciding what to do next. Figure K-1 shows a typical family of curves. The minimum error occurs at 33.670 background but it is obvious that there is some curvature in that curve as well as the background of 29.929 being quite close to having a straight portion. It is therefore advisable to recalculate the variances with a narrower background range centered about the best current background. A second plot is generally not necessary since the linearities are too close for the eye to accurately differentiate.

The program uses 100 range steps to calculate the variances and searches for a linear region in the last 50 of those steps. It is possible that the range chosen is too large or too narrow to get a linear region. The operator can decide from the first plot and

experience whether or not to change the starting range.

A new background is requested, a series by adding a finite increment and a single one by entering an increment of Ø:

```
ENTER DESIRED AVERAGE BACKGROUND AND BKG INCREMENT
   TO TERMINATE THIS LOOP ENTER "Ø" INCREMENT
```

The process of calculating a family of curves and plotting will be continued until a single background is chosen. At this point the plotting questions for axes scales are asked (see section 3.2.3) and the variance-range curve with a line through the last half is drawn.

When a carriage return is hit after the slope and intercept of that line are printed:

```
THE SLOPE IS  Ø.ØØØØØ +/-  Ø.ØØØØØ
WITH AN INTERCEPT OF -Ø.ØØØØØ +/-  Ø.ØØØØØ

DOES THIS HAVE A GOOD "LINEAR" REGION?
```

The last question allows you to chose another portion of that curve by entering the range values or with cursors if your terminal is so equiped.

When you do have a good linear region the program assumes you are finished with these particular conditions and prints the available options:

```
WHAT DO YOU WANT TO DO?

  Ø  -  GO TO ANOTHER REGION OF THIS DATA SET (DEFAULT)
  1  -  RETURN TO MAIN PROGRAM OPTION SECTION
  2  -  RECALCULATE CENTROID USING THE CURRENT BKG
  3  -  RECALCULATE VARIANCES
```

4 - REPLOT FINAL VARIANCE AND EXTRAPOLATED STRAIGHT LINE

The first option is probably the most commonly used one which returns the user to the top of this method, requesting an initial amd final two-theta range. The next option, as it says, returns the program to the main program Option section where the operator can chose any of those options (see section 3.2.2). Recalculating the centroid using the current background is not an option used very frequently; the centroid calculations are not very sensitive to the background and this option should be called only when the background originally used is very much different from the final background level. Option "3" will be used when the background used for the final single plot is unsatisfactory. Single or family of variance-range curves can be calculated. The last option should be called only if the plotting scales used in the single background plot are unsatisfactory. It can also be used to find a new linear range if needed.

3.2.7 Second Phase Intensity Stripping

If no second phase was assigned then an error message will appear when you call option 6. However, if there is a second phase then the option will begin:

```
ONCE STRIPPED FROM THE SCAN, THE INTENSITY FROM THE
   SECOND PHASE IS LOST IRREVOCABLY.

DO YOU STILL WANT TO STRIP THE SECOND PHASE?  Y/N
```

If you answer no to this question you will return to the option section. A yes will ask for two common baseline diffraction angles for the second phase scan and the sample scan.

```
ENTER TWO BASELINE ANGLES (SUCH AS THE FIRST AND LAST ANGLES)
```

Any two angles where the intensity in the scans reach a minimum will do. The program will then scale the second phase at its maximum intensity to the sample scan and subtract that to produce a "stripped" scan which can then be analyzed in the same way the original scan was analyzed. The program will list any angles where the scaled second phase scan is higher than the composite scan and ask if you want to enter a different scale factor. If you have already stripped the second phase scan, here is a place where you can add it back by entering a negative scale factor equal in magnitude to the original scale factor.

Figure 4 shows an unstripped scan and the same scan once stripped of the second phase.

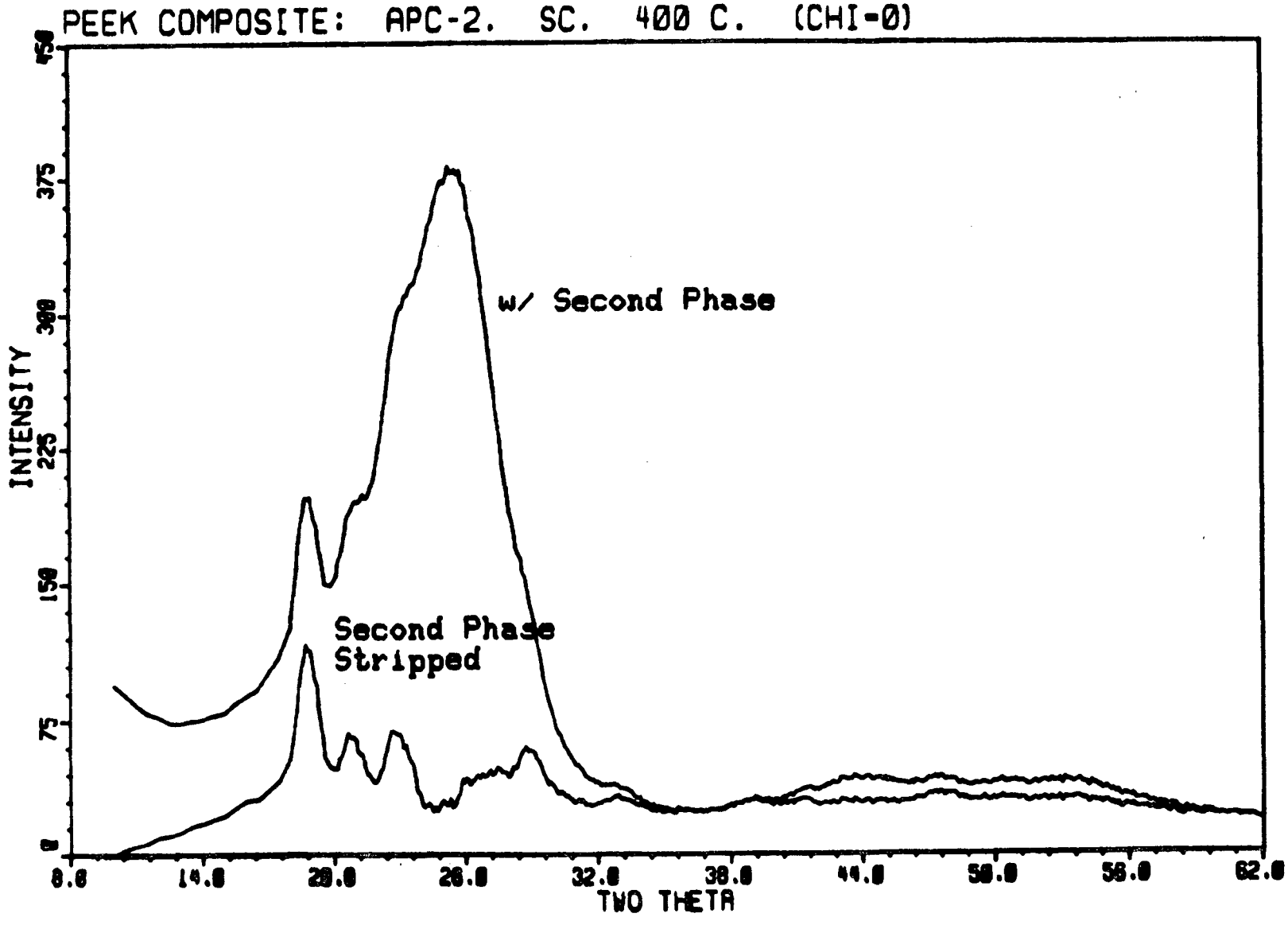


Figure 4. A diffraction scan with intensity from a second phase and with the second phase intensity stripped away.

SECTION 4

FUTURE WORK

Like most programs, DIFF will likely undergo more changes to fit the needs of the users, but it is expected that the basic operation will remain more or less the same. It is planned that the general user friendliness of the program will be maintained or improved so that any future additions can be used by any user who is familiar with the current version.

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APPENDIX A

TYPICAL INPUT DATA FILE

```
HEAD PEEK DIFFRACTION FOR JULY 84        Start of Predata
INTR
POLM .7986
PICKER
BACK
AMOR 1
CCOM 3
ABSL 0.440 1.076 1.012 1.069 0.793 0.826 0.811 0.787 0.382 0.436
NCAR 19
NHYD 12
NOXY 03
LEVP 1
END                                      End of Predata
/HD
AMORPHOUS PEEK  7/28/84                  1st Data set
/TH                                      (amorphous scan)
 TH=10  DLTH=.1  TH=32  DLTH=1  TH=60  DLTH=0
 12.75 12.61 13.08 12.92 13.36 13.56 13.67 14.14 14.59 14.52
 14.97 15.14 15.63 15.76 16.08 16.45 16.95 17.08 17.67 17.85
 18.24 18.60 18.93 19.73 20.10 20.61 21.15 21.59 21.99 22.65
 23.31 23.78 24.31 24.89 25.62 26.26 26.85 27.69 28.40 28.99
 30.13 30.71 31.65 32.56 33.45 34.09 35.12 35.99 36.72 38.36
    .
    .   12 lines of intensities (counts per second)
    .
 26.17 25.73 25.85 25.52 25.00 24.90 24.41 24.41 24.44 24.44
 23.65 23.31 22.83 23.18 23.07 22.68 22.46 22.27 22.29 21.63
 21.52 21.48 20.84 21.29 20.35 20.93 20.26 20.52 20.60 20.22
 19.84 19.68 19.53 18.79 18.74 19.00 18.24 18.32 17.96 17.98
 17.56 17.33 17.48 17.48 16.94 16.96 16.58 16.74 16.75 16.15
 15.72 14.85 13.46 12.66 11.63 11.22 11.26 11.56 11.68 12.07
 12.83 12.57 11.98 12.15 11.80 11.52 10.95  9.92  9.25  8.94
  8.44  7.76  7.50  6.97  6.93  6.11  5.83  5.78  5.56
BACKGROUND FOR JULY 84                   2nd Data set
/TH                                      (background scan)
 TH=10  DLTH=1  TH=60  DLTH=0
  1.58  1.46  1.16  1.14  1.00  0.89  0.87  0.72  0.72  0.65
  0.57  0.57  0.46  0.41  0.37  0.38  0.36  0.28  0.33  0.25
  0.25  0.22  0.26  0.18  0.16  0.19  0.14  0.14  0.18  0.15
  0.15  0.14  0.12  0.12  0.12  0.11  0.08  0.08  0.08  0.06
  0.05  0.07  0.09  0.08  0.08  0.10  0.10  0.08  0.08  0.08
  0.06
/HD                                      3rd Data set
PEEK RESIN                               (2nd sample scan)
/TH
 TH=10  DLTH=.5  TH=16  DLTH=.1  TH=32  DLTH=1  TH=60  DLTH=0
 10.91 12.58 13.17 14.62 15.91 16.97 18.56 19.99 23.82 27.30
 30.03 33.14 38.59 39.16 40.30 41.34 40.32 43.67 42.93 45.31
 45.13 47.15 47.37 49.49 51.34 51.78 52.47 53.96 56.03 57.19
    etc.
```

APPENDIX B

INITIAL OUTPUT FROM RUNNING THE "DIFF" PROGRAM

```
OK, SEG #DIFF

ENTER DATA FILE-NAME
PEEK-7

***  PREDATA INSTRUCTIONS FOLLOW  ***

   YOU ARE IN THE INTERACTIVE MODE
   POLARIZATION CONSTANT SET TO:  Ø.7986
   PICKER FACS-1 DATA
   BACKGROUND SCAN IS PRESENT
   AMORPHOUS SCAN IS DATA SET NUMBER: 1
   COMPTONS SCATTERING OPTION: 3
   FILM ut VALUES READ IN:
      DATA SET  1 HAS ut =  Ø.44ØØ    (no μt for background, data
      DATA SET  2 HAS ut =  1.Ø76Ø    set numbers do not count the
      DATA SET  3 HAS ut =  1.Ø12Ø    background set)
      DATA SET  4 HAS ut =  1.Ø69Ø
      DATA SET  5 HAS ut =  Ø.793Ø
      DATA SET  6 HAS ut =  Ø.826Ø
      DATA SET  7 HAS ut =  Ø.811Ø
      DATA SET  8 HAS ut =  Ø.787Ø
      DATA SET  9 HAS ut =  Ø.382Ø
      DATA SET 1Ø HAS ut =  Ø.436Ø
   NCAR  19
   NHYD  12
   NOXY   3
   PRINT OPTION: 1

WHAT TYPE OF TERMINAL ARE YOU AT?
   -1 = NON-GRAPHICS
    Ø = TEKTRONIX
    1 = AED 1Ø24
Ø

     screen erases
```

```
**************************************************************************

 PEEK DIFFRACTION FOR JULY 84

AMORPHOUS SCAN ASSIGNMENT COMPLETE

**************************************************************************


AMORPHOUS PEEK  7/28/84
WED, FEB Ø5 1985   Ø9:35:24


THE INCIDENT BEAM WAVELENGTH=1.5418 ANGSTROMS
   #HYD= 12       #CAR= 19       #NIT=  Ø
   #OXY=  3       #FLO=  Ø       #CHL=  Ø
   #SUL=  Ø       #BRO=  Ø       #PHO=  Ø
 CCOMPT=    Ø.78 EVALUATED FROM  THIS DATA SET, AT TWO THETA= 6Ø.ØØ
 ABSORPTION CORRECTIONS BASED ON uT= Ø.44ØØ
INTEGRATED INTENSITY=    652.241 AVERAGE INTENSITY=   12.336
OVER TWO THETA RANGE OF  1Ø.ØØ TO  6Ø.ØØ DEGREES
     2Ø1 DATA POINTS

***   END OF SCAN   ***

**************************************************************************


***  PLOTTING BEGINS  ***


DO YOU WANT TO PLOT THIS DATA SET? Y/N
N


OPTIONS ARE:
   1 = CONTINUE TO NEXT DATA SET
   2 = GO TO PLOTTING SECTION
   3 = WEIGHT FRACTION CRYSTALLINITY CALCULATIONS
   4 = CURVE FITTING CALCULATIONS
   5 = LINE BROADENING CALCULATIONS
   6 = SECOND PHASE STRIPPING
   7 = EXIT PROGRAM
1

     screen erases
```

```
**************************************************************************


PEEK RESIN
WED, FEB 05 1985   09:45:16


THE INCIDENT BEAM WAVELENGTH=1.5418 ANGSTROMS
   #HYD= 12       #CAR= 19       #NIT=  0
   #OXY=  3       #FLO=  0       #CHL=  0
   #SUL=  0       #BRO=  0       #PHO=  0
 CCOMPT=    1.82 EVALUATED FROM  THIS DATA SET, AT TWO THETA= 60.00
 ABSORPTION CORRECTIONS BASED ON uT= 1.0760
INTEGRATED INTENSITY=   1522.370 AVERAGE INTENSITY=   30.448
OVER TWO THETA RANGE OF  10.00 TO  60.00 DEGREES
     201 DATA POINTS

***   END OF SCAN   ***

**************************************************************************


***  PLOTTING BEGINS  ***


DO YOU WANT TO PLOT THIS DATA SET? Y/N
```

A "Y" will send the user to the Plotting section (Appendix D)

A "N" will send the user to the Option section (3.2.2)

APPENDIX C

EXAMPLE OF INTENSITY CORRECTION OUTPUT

This will be written on FIT.INT with print option 1 or 3.

TWO THETA	UNCORRECTED INTENSITY	CORRECTED INTENSITY	AIR SCATTER INTENSITY	INCOHERENT FACTOR	ABSORPTION CORRECTION
10.00	10.9100	11.0347	0.0000	0.35490	1.00030
10.50	12.5800	11.2032	1.5200	0.37935	1.00033
11.00	13.1700	11.8832	1.4600	0.40432	1.00036
11.50	14.6200	13.5384	1.3100	0.42978	1.00040
12.00	15.9100	15.0373	1.1600	0.45572	1.00043
12.50	16.9700	16.1635	1.1500	0.48212	1.00047
13.00	18.5600	17.8414	1.1400	0.50896	1.00051
13.50	19.9900	19.4249	1.0700	0.53622	1.00055
14.00	23.8200	23.4996	1.0000	0.56388	1.00060
14.50	27.3000	27.2172	0.9450	0.59194	1.00064
15.00	30.0300	30.1759	0.8900	0.62037	1.00069
15.50	33.1400	33.5013	0.8800	0.64915	1.00074
16.00	38.5900	39.2921	0.8700	0.67827	1.00080
16.10	39.1600	39.9243	0.8550	0.68413	1.00081
16.20	40.3000	41.1536	0.8400	0.69000	1.00082
16.30	41.3400	42.2797	0.8250	0.69589	1.00083
16.40	40.3200	41.2499	0.8100	0.70179	1.00084
16.50	43.6700	44.7981	0.7950	0.70770	1.00085
16.60	42.9300	44.0623	0.7800	0.71363	1.00086
16.70	45.3100	46.5988	0.7650	0.71956	1.00087
16.80	45.1300	46.4513	0.7500	0.72551	1.00088
16.90	47.1500	48.6143	0.7350	0.73147	1.00089
17.00	47.3700	48.8884	0.7200	0.73744	1.00091
17.10	49.4900	51.1450	0.7200	0.74342	1.00092
17.20	51.3400	53.1203	0.7200	0.74942	1.00093
17.30	51.7800	53.6139	0.7200	0.75542	1.00094
17.40	52.4700	54.3714	0.7200	0.76144	1.00095
17.50	53.9600	55.9732	0.7200	0.76746	1.00096
17.60	56.0300	58.1888	0.7200	0.77350	1.00098
17.70	57.1900	59.4469	0.7200	0.77955	1.00099
17.80	59.4000	61.8154	0.7200	0.78561	1.00100
17.90	60.1500	62.6445	0.7200	0.79167	1.00101
18.00	63.6800	66.4136	0.7200	0.79775	1.00102
.					
.					
.					
52.00	8.5400	12.6237	0.0900	2.58994	1.01456
53.00	9.7900	14.8019	0.0800	2.62154	1.01544
54.00	8.1500	12.4130	0.0800	2.65201	1.01635
55.00	7.6000	11.6845	0.1000	2.68137	1.01731
56.00	6.4500	9.9753	0.1000	2.70742	1.01832
57.00	6.9100	10.9384	0.0800	2.73217	1.01938
58.00	6.4500	10.3323	0.0800	2.75592	1.02049
59.00	5.8000	9.3765	0.0800	2.77872	1.02165
60.00	6.0100	9.9313	0.0600	2.80061	1.02287

APPENDIX D

PLOTTING QUESTIONS AND PLOTS

Enter Option 2 and after the screen erases:

```
WHAT DO YOU WANT TO PLOT?  TYPE APPROPRIATE NUMBER
    1=INTENSITY VERSUS TWO THETA
    2=INTENSITY VERSUS S, WHERE S=1/d
    3=(S**2)*INTENSITY VERSUS S
1
DO YOU WISH TO CHANGE THE X OR Y AXIS LENGTH?  Y/N
N
DO YOU WANT THE COMPUTER TO CHOOSE THE AXIS SCALE?  Y/N
N
XMIN=  10.0000 XMAX=  59.9997 XDELTA=   5.5555
TYPE IN XMIN AND XMAX ON SAME LINE...
8 62
XMIN=   8.0000 XMAX=  62.0000 XDELTA=   6.0000
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=   9.3765 YMAX= 195.0297 YDELTA=  30.9422
0 200
YMIN=   0.0000 YMAX= 200.0000 YDELTA=  33.3333
DO YOU WISH TO CHANGE THESE?  Y/N
Y
TYPE IN YMIN AND YMAX ON SAME LINE...
0 240
YMIN=   0.0000 YMAX= 240.0000 YDELTA=  40.0000
DO YOU WISH TO CHANGE THESE?  Y/N
N
HOW DO YOU WANT THE DATA DISPLAYED? TYPE   N
    N<0 DRAWS A SYMBOL AT EVERY NTH POINT
    N=0 CONNECTS ALL POINTS WITH A STRAIGHT LINE
    N>0 DRAWS A SYMBOL AT EVERY NTH POINT AND CONNECTS THE POINTS WITH
        A LINE
0

DO YOU WISH TO DRAW LINES ON YOUR PLOT?  Y/N
Y
TYPE IN THE LINE SPACING IN INCHES FOR X AND Y AXES, ON THE SAME LINE
1 .5
START PLOT?  Y/N
Y
```

The screen erases and the plot is generated (see Figure D-1).

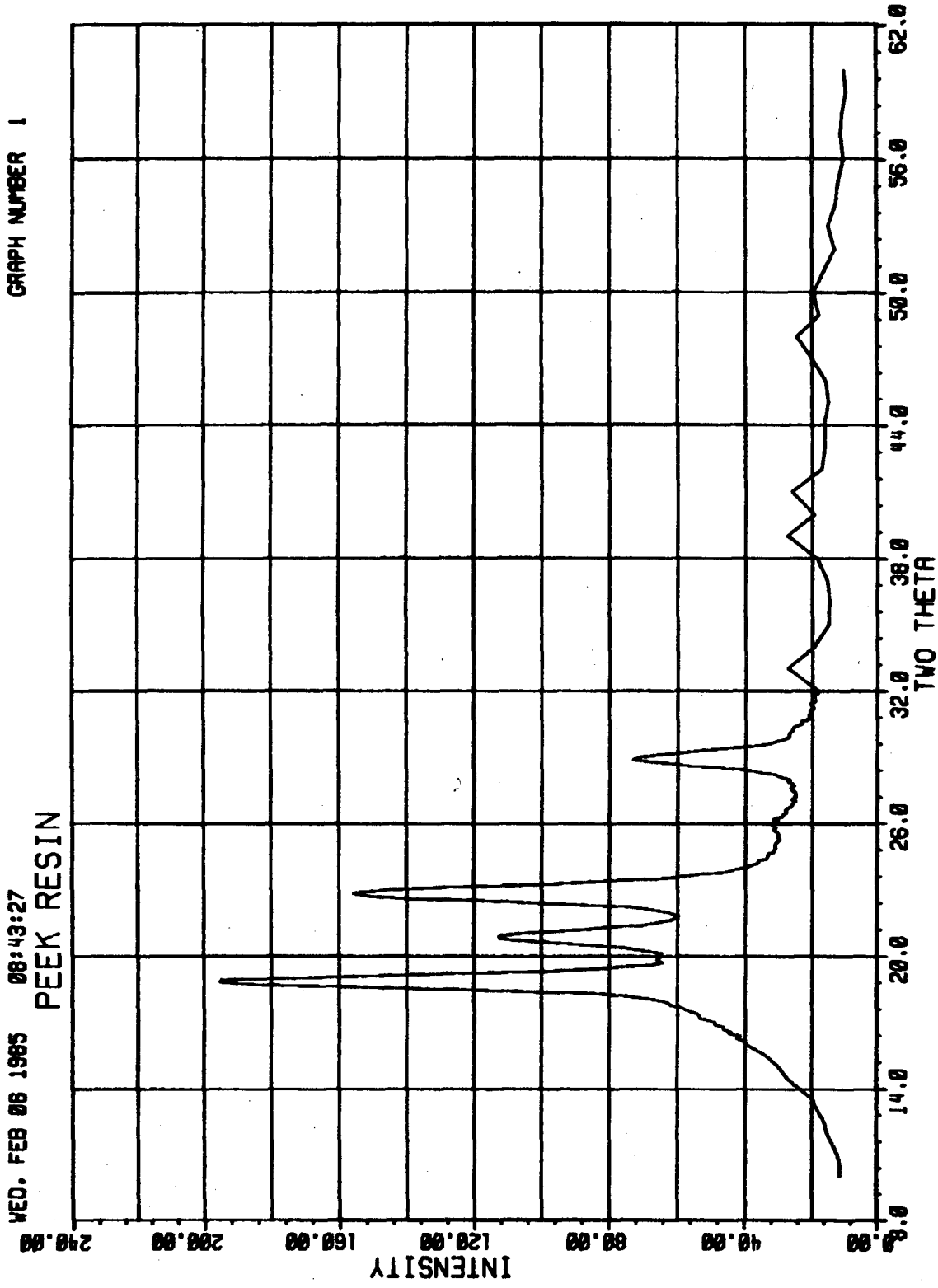

Figure D-1. Sample plot of intensity versus two-theta.

After the plot is finished a CR will erase the screen and print:

DO YOU WANT A CALCOMP PLOT? Y/N
N

The program will then return to the Option section (3.2.2). Figure D-2 shows the same data as Figure D-1 but plotted without lines, symbols only (N=-1), and plot option 2 of Intensity versus s. Figure D-3 is a plot of the same data, this time with plot option 3 of I x s^2 versus s and the data point symbols connected by lines (N=1).

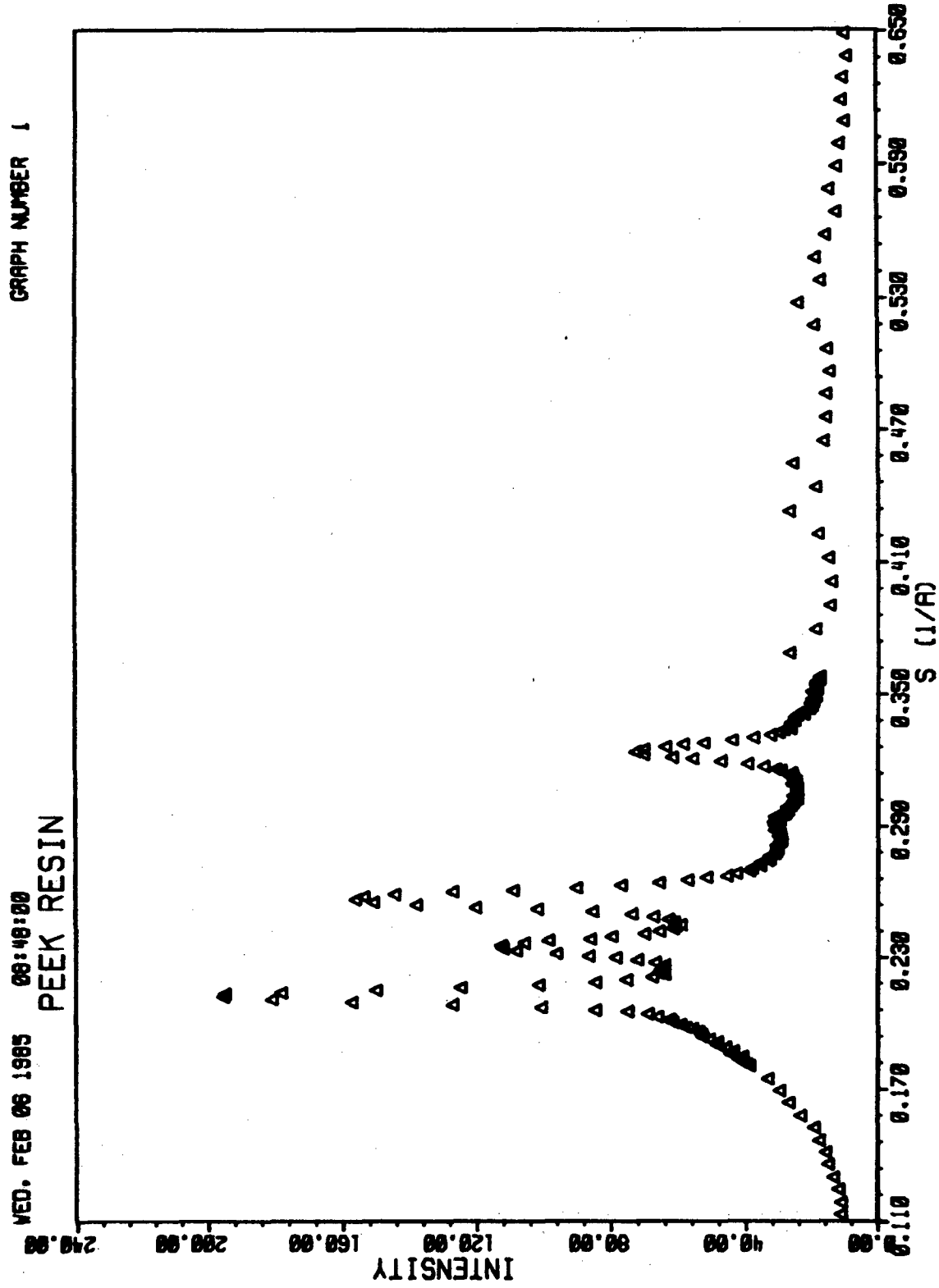

Figure D-2. Sample plot of intensity versus s.

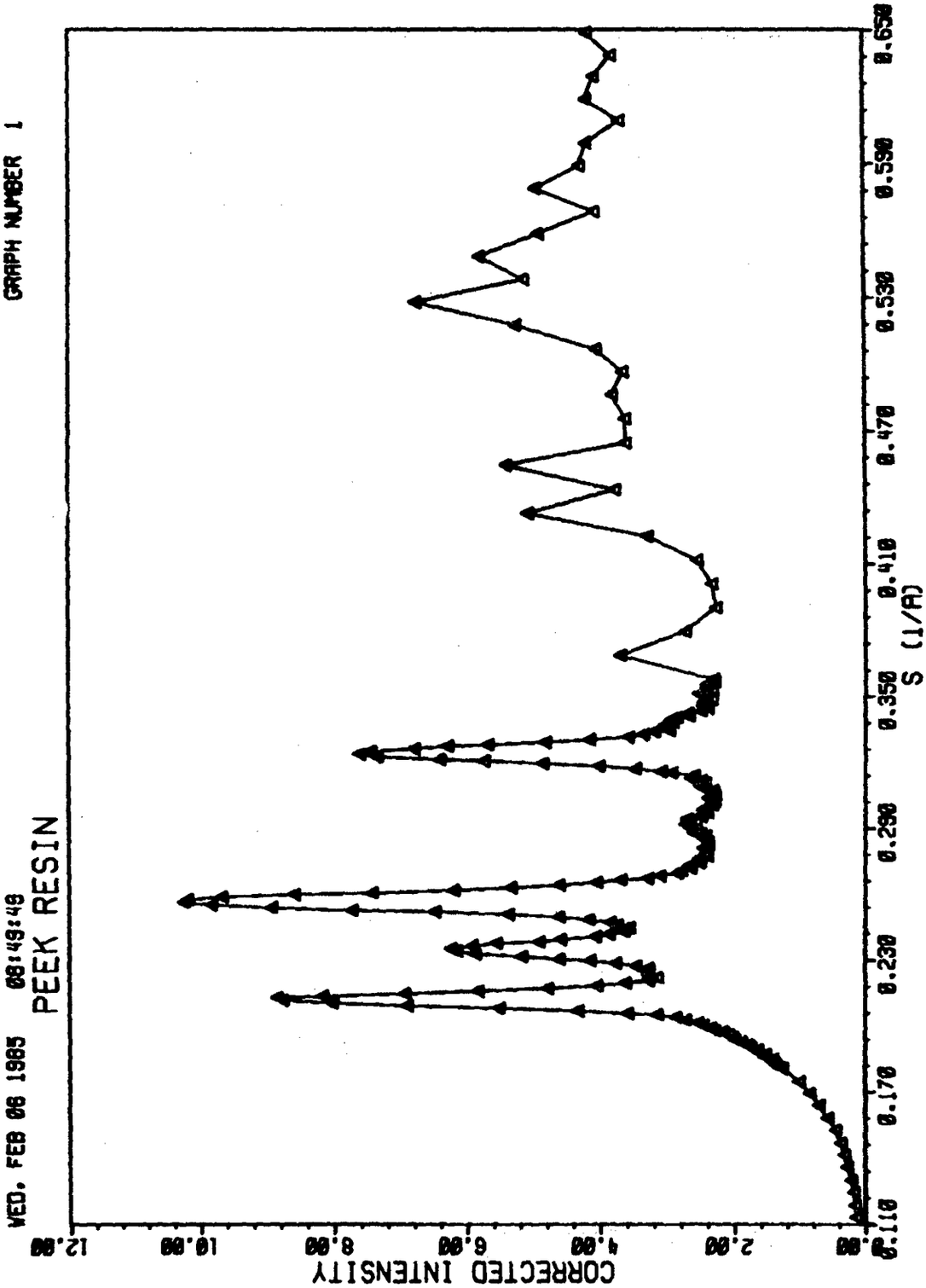

Figure D-3. Sample plot of Ruland corrected intensity ($I \times s^2$) versus s.

APPENDIX E

RULAND DEGREE OF CRYSTALLINITY MEASUREMENTS

Enter Option 3 and after the sceen erases:

```
DO YOU WANT THE ORIGINAL RULAND ANALYSIS (Y),
   OR THE VONK MODIFICATION (DEFAULT)
Y

DOES YOUR TERMINAL HAVE CURSORS?  Y/N
N
TYPE IN THE NUMBER OF REGIONS YOU WISH TO ANALYZE
12
WARNING--NUMBER OF REGIONS= 12, WHICH EXCEEDS MAXIMUM OF 10.
   TRY AGAIN
TYPE IN THE NUMBER OF REGIONS YOU WISH TO ANALYZE
5
TYPE IN THE VALUES FOR So----Sn YOU WISH TO USE
0.113
0.283
0.305
0.356
0.390
0.496

POINT =  1  S = 0.11306  Is**2 =  0.14104
POINT =  2  S = 0.28297  Is**2 =  2.39434
POINT =  3  S = 0.30502  Is**2 =  2.29623
POINT =  4  S = 0.35646  Is**2 =  2.28173
POINT =  5  S = 0.39007  Is**2 =  3.56795
POINT =  6  S = 0.49641  Is**2 =  3.94254

DO YOU WANT TO SEE A PLOT OF THE REGIONS YOU HAVE CHOSEN?  Y/N
N
```

See Appendix F for an example the plot of regions.

```
ARE YOU SATISFIED WITH THESE REGIONS?  Y/N
Y

TYPE IN DISORDER PARAMETER (k) RANGE AND DELTAk
   THE MAX # OF ks IS 10
0,9,1

DISORDER PARAMETER= 0.000
  So   -   Sp          DEGREE OF CRYSTALLINITY      BIG K
0.1187 - 0.3061           0.473                     1.0000
0.1187 - 0.3565           0.422                     1.0000
0.1187 - 0.3901           0.401                     1.0000
0.1187 - 0.4964           0.457                     1.0000
0.1187 - 0.6090           0.480                     1.0000

COEFFICIENT OF VARIATION (%)                  9.383

MEAN WEIGHT FRACTION CRYSTALLINITY            0.442
```

```
DISORDER PARAMETER= 1.000
  So   -   Sp          DEGREE OF CRYSTALLINITY      BIG K
0.1187 - 0.3061           0.421                     1.4734
0.1187 - 0.3565           0.373                     1.6454
0.1187 - 0.3901           0.350                     1.7808
0.1187 - 0.4964           0.408                     2.3191
0.1187 - 0.6090           0.433                     3.0687

COEFFICIENT OF VARIATION (%)                  8.721

MEAN WEIGHT FRACTION CRYSTALLINITY            0.391

    .
    .
    .

DISORDER PARAMETER= 9.000
  So   -   Sp          DEGREE OF CRYSTALLINITY      BIG K
0.1187 - 0.3061           0.421                     1.6385
0.1187 - 0.3565           0.472                     1.8800
0.1187 - 0.3901           0.406                     2.0723
0.1187 - 0.4964           0.407                     2.8463
0.1187 - 0.6090           0.432                     3.9240

COEFFICIENT OF VARIATION (%)                 16.429

MEAN WEIGHT FRACTION CRYSTALLINITY            0.427


DO YOU WANT TO SEE A PLOT OF VARIATION FACTOR VERSUS DISORDER
 PARAMETER k?  Y/N
Y

XMIN=    0.0000 XMAX=    9.0000 XDELTA=    1.0000
TYPE IN XMIN AND XMAX ON SAME LINE...
0. 9.
XMIN=    0.0000 XMAX=    9.0000 XDELTA=    1.0000
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=    3.3221 YMAX=   16.4293 YDELTA=    2.1845
TYPE IN YMIN AND YMAX ON SAME LINE...
0 24
YMIN=    0.0000 YMAX=   24.0000 YDELTA=    4.0000
DO YOU WISH TO CHANGE THESE?  Y/N
N
```

The screen will erase and Figure E-1 will be plotted.

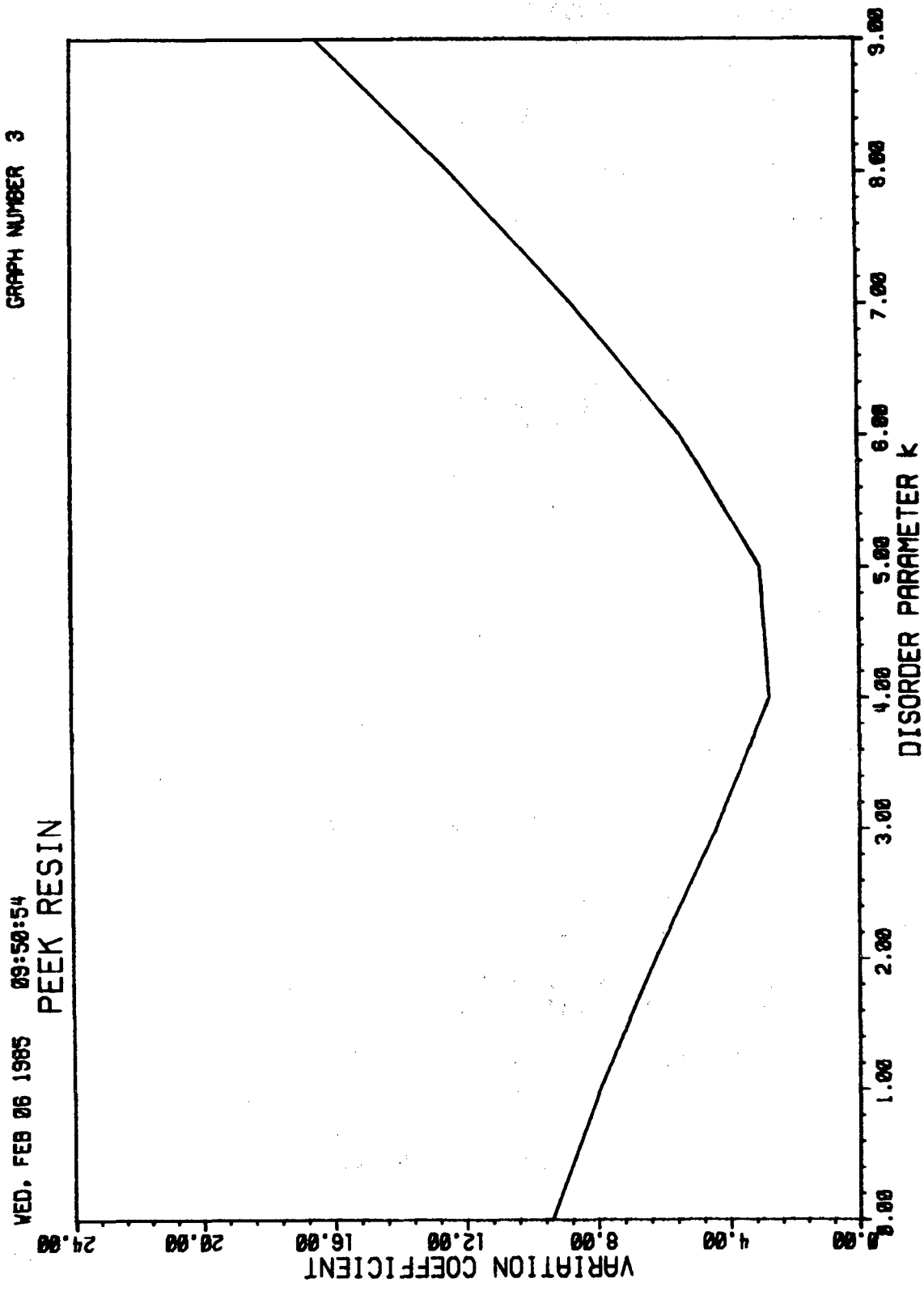

Figure E-1. Ruland plot of variance coefficient versus disorder parameter k.

Hitting a carriage return will erase the screen:

DO YOU WANT TO CHOOSE A DIFFERENT DISORDER PARAMETER REGION? Y/N
N

DO YOU WISH TO TRY DIFFERENT VALUES FOR So----Sn? Y/N
N

*** WEIGHT FRACTION CRYSTALLINITY CALCULATIONS ARE FINISHED ***

The program then returns to the Option section (3.2.2)

APPENDIX F

VONK'S VARIATION FOR DEGREE OF CRYSTALLINITY

Enter Option 3 and after the sceen erases:

```
DO YOU WANT THE ORIGINAL RULAND ANALYSIS (Y),
   OR THE VONK MODIFICATION (DEFAULT)
N

DOES YOUR TERMINAL HAVE CURSORS?  Y/N
Y
TYPE IN THE NUMBER OF REGIONS YOU WISH TO ANALYZE
5
YOU ARE IN THE CURSOR MODE.


***  PREPARE TO PLOT ***

XMIN=   Ø.1124 XMAX=   1.1987 XDELTA=   Ø.1207
TYPE IN XMIN AND XMAX ON SAME LINE...
Ø.11 Ø.65
XMIN=   Ø.1100 XMAX=   Ø.6500 XDELTA=   Ø.Ø6ØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=   Ø.1765 YMAX=  1Ø.5297 YDELTA=   1.7422
TYPE IN YMIN AND YMAX ON SAME LINE...
Ø 12.
YMIN=   Ø.ØØØØ YMAX=  12.ØØØØ YDELTA=   2.ØØØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
```

A plot similar to Figure D-3 will be drawn and the cursors will appear on the screen. The 5 region's borders are defined with the vertical cursor. The screen will erase:

```
POINT =  1  S = Ø.11306  Is**2 =  Ø.14104
POINT =  2  S = Ø.28297  Is**2 =  2.39434
POINT =  3  S = Ø.3Ø5Ø2  Is**2 =  2.29623
POINT =  4  S = Ø.35646  Is**2 =  2.28173
POINT =  5  S = Ø.39ØØ7  Is**2 =  3.56795
POINT =  6  S = Ø.49641  Is**2 =  3.94254

DO YOU WANT TO SEE A PLOT OF THE REGIONS YOU HAVE CHOSEN?  Y/N
Y
```

The screen will erase and Figure F-1 will be plotted.

Figure F-1. Sample plot of $I s^2$ versus s curves with amorphous (//), crystalline (\\), and baseline (||) regions highlighted.

Hitting a carriage return will erase the plot:

```
ARE YOU SATISFIED WITH THESE REGIONS?  Y/N
Y

CRYSTALLINITY =  Ø.532 +/-  Ø.ØØ2

DISORDER PARAMETER (k) =  3.625 +/-  Ø.Ø5Ø

    So  -  Sp       R of TOT/CR   Sp **2
Ø.11306 - Ø.28297     3.Ø8628     Ø.3Ø5Ø2
Ø.11306 - Ø.3Ø5Ø2     3.Ø4165     Ø.35646
Ø.11306 - Ø.35646     3.14979     Ø.39ØØ7
Ø.11306 - Ø.39ØØ7     3.48116     Ø.49641
Ø.11306 - Ø.49641     3.72174     Ø.6Ø899

DO YOU WANT TO SEE A PLOT OF TOTAL TO CRYSTAL INTENSITY RATIO vs Sp**2
Y

XMIN=   Ø.3Ø5Ø XMAX=   Ø.6Ø9Ø XDELTA=   Ø.Ø5Ø7
TYPE IN XMIN AND XMAX ON SAME LINE...
Ø. Ø.9
XMIN=   Ø.ØØØØ XMAX=   Ø.9ØØØ XDELTA=   Ø.Ø6ØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=   3.Ø416 YMAX=   3.7217 YDELTA=   Ø.1133
TYPE IN YMIN AND YMAX ON SAME LINE...
Ø 4.5
YMIN=   Ø.ØØØØ YMAX=   4.5ØØØ YDELTA=   Ø.75ØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
```

The screen will erase and Figure F-2 will be plotted. Hitting a carriage return erases the plot:

```
DO YOU WISH TO TRY DIFFERENT VALUES FOR So----Sn?  Y/N
N
***  WEIGHT FRACTION CRYSTALLINITY CALCULATIONS ARE FINISHED  ***
```

The program then returns to the Option section (3.2.2)

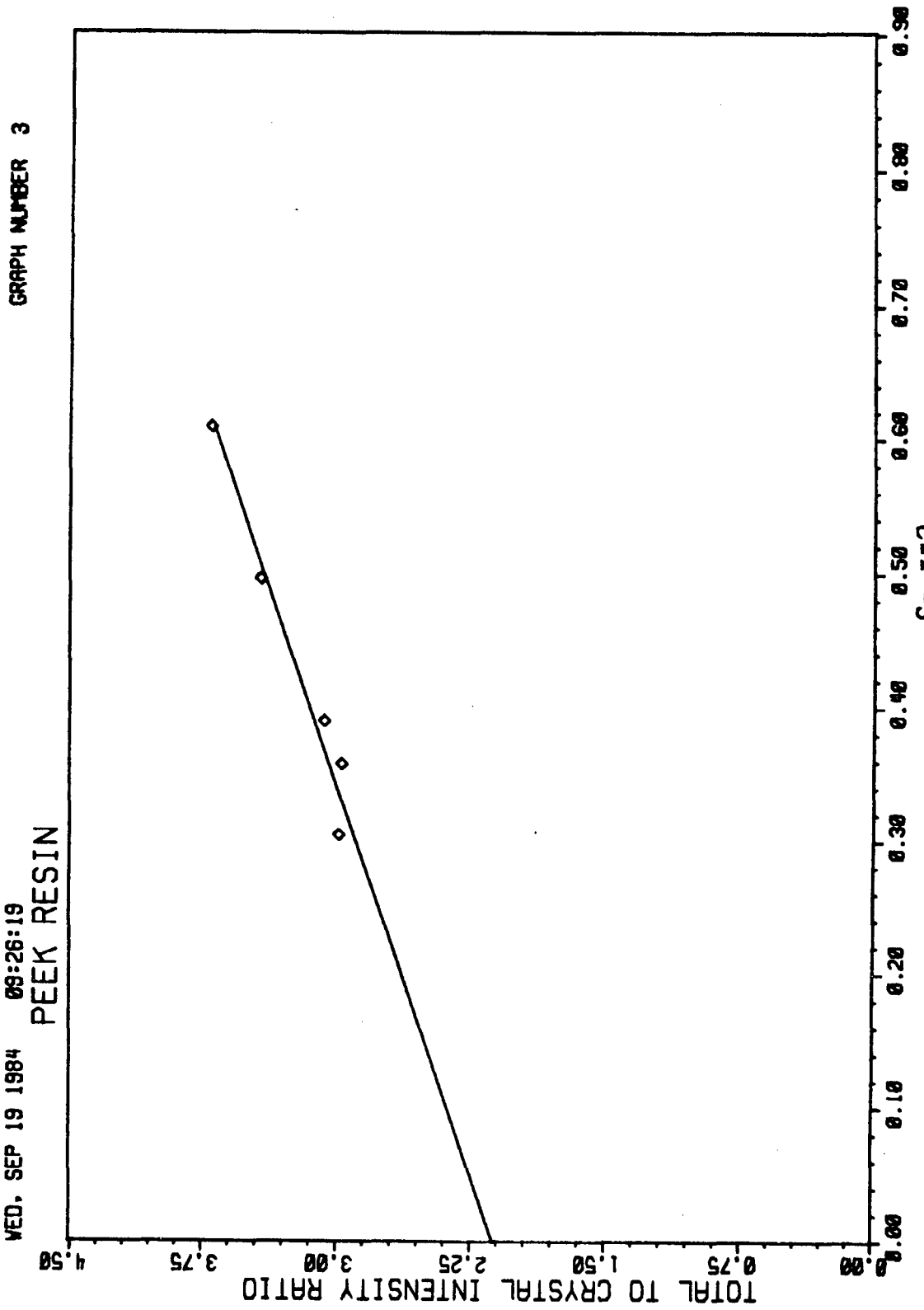

Figure F-2. Vonk plot of $R(s_p^2)$ versus s_p^2.

APPENDIX G

CURVE FITTING AND SUBSEQUENT PLOTS OF CURVES

Enter Option 4 and after the screen erases:

```
DO YOU WANT TO FIT THIS DATA?
Y                                        (No is default)

FITTED CURVES?
   Ø=I S**2  VS S
   1=I VS S
   2=I VS 2 THETA
Ø

WHAT TYPE FUNCTION(S)?
   Ø=MIXED GAUSSIAN AND CAUCHY
   1=PEARSON TYPE VII
   2=GAUSSIAN
   3=CAUCHY
1

WEIGHT FACTOR?
   Ø=SQRT(Y(I)/YMAX)
   1=1/Y(I)
   2=UNITY
Ø

FROM WHAT INITIAL POSITION TO WHAT FINAL POSITION?
.11 .355

THE MIN POS IS Ø.11306  THIS IS THE   1 DATA POINT
THE MAX POS IS Ø.35537  THIS IS THE 171  DATA POINT

THE TOTAL NUMBER OF DATA POINTS TO BE FITTED IS 171
THE AVERAGE S IS    Ø.25965 AND THE AVERAGE RCI IS   3.54544

TYPE THE NUMBER OF BASELINE POINTS (2 TO 6)
2

TYPE THE APPROX. POSITION AND INTENSITY OF THE BASELINE
 1 FIXES THE INTENSITY, Ø DOES NOT   EG:
 .123 Ø Ø.1234
 .345 Ø 1.2345
 .11 1 Ø.
 .355 Ø .5

DO YOU WANT TO FIT THE AMORPHOUS SCAN TO THIS DATA SET?
Y

TYPE INITIAL AMORPHOUS PEAK HEIGHT FOR FITTING, EG:
2.123
2.5

TYPE THE NUMBER OF PEAKS TO BE FITTED (MAX OF 12)
5
```

```
  PEAK POS     INT AT MAX      FW-HM      EXPONENT
Ø .212  Ø 4.123  1 .ØØ6  Ø .5  FOR EXAMPLE
Ø .345  Ø 9.876  1 .ØØ12  Ø 4.Ø
Ø .21 Ø 5. Ø .ØØ6 Ø 4.
Ø .235 Ø 3. Ø .ØØ7 Ø 4.
Ø .257 Ø 7. Ø .ØØ8 Ø 4.
Ø .29 Ø .5 Ø .ØØ6 Ø 4.
Ø .32 Ø 4. Ø .ØØ8 Ø 4.
```

screen will erase then:

```
**********************************************************
* PEEK RESIN                                             *
*                  WEDS, NOV Ø7 1984     Ø9:55:18        *
**********************************************************


WEIGHT FACTOR=SQRT(Y(I)/YMAX)

FOR ITERATION >  1  SE =    93.6759 X 1Ø E-3
FOR ITERATION >  2  SE =    27.Ø344 X 1Ø E-3
FOR ITERATION >  3  SE =     8.3667 X 1Ø E-3
FOR ITERATION >  4  SE =     1.858Ø X 1Ø E-3
FOR ITERATION >  5  SE =     Ø.8753 X 1Ø E-3
FOR ITERATION >  6  SE =     Ø.8666 X 1Ø E-3
FOR ITERATION >  7  SE =     Ø.8352 X 1Ø E-3
FOR ITERATION >  8  SE =     Ø.8223 X 1Ø E-3
FOR ITERATION >  9  SE =     Ø.8127 X 1Ø E-3
FOR ITERATION > 1Ø  SE =     Ø.8Ø93 X 1Ø E-3


THE FINAL FITTING PARAMETERS AND OTHER INFORMATION ARE GIVEN BELOW:

          PEAK POS  D-SPACING    INT AT MAX   AREA      . . .
AMOR    Ø  Ø.24229  4.12728    Ø  2.5637Ø  Ø.7474Ø    . . . This and the
PK 1    Ø  Ø.21243  4.7Ø733    Ø  6.23796  Ø.1Ø652    . . . next block
PK 2    Ø  Ø.23504  4.25457    Ø  3.33638  Ø.Ø6756    . . . will be
PK 3    Ø  Ø.25691  3.89242    Ø  7.67952  Ø.17313    . . . printed on
PK 4    Ø  Ø.2918Ø  3.427Ø6    Ø  Ø.25899  Ø.ØØ332    . . . same line.
PK 5    Ø  Ø.32419  3.Ø8463    Ø  5.12417  Ø.11Ø15    . . .

  . . .       FW-HM  INTGRL BRDTH      EXPONENT
  . . .  Ø   Ø.Ø8Ø55   Ø.29153    1   -1.ØØ
  . . .  Ø   Ø.ØØ755   Ø.Ø1Ø8    Ø    3.88
  . . .  Ø   Ø.ØØ87Ø   Ø.Ø2Ø25   Ø    2.79
  . . .  Ø   Ø.ØØ97Ø   Ø.Ø2254   Ø    2.82
  . . .  Ø   Ø.ØØ6Ø3   Ø.Ø1283    1 5555.ØØ
  . . .  Ø   Ø.ØØ922   Ø.Ø215Ø   Ø    2.76


LEVPR=2; THE FITTED AND EXPERIMENTAL DATA WILL BE WRITTEN ON "FIT.DAT".
ALL FITTING PARAMETERS ARE WRITTEN ON "FIT.PAR".
```

```
BASELINE POSITIONS AND INTENSITIES
1    Ø.1131  1 Ø.ØØØØØ
2    Ø.3554  Ø Ø.77594
BASELINE AREA =    Ø.Ø94Ø1

DO YOU WANT A PRINT-OUT OF THE FITTED DATA?
N   (a Yes response gets a listing of the data as shown in Appendix I)

DO YOU WANT A PLOT OF THIS FIT?
Y

XMIN=   Ø.1131 XMAX=   Ø.3554 XDELTA=   Ø.2693
TYPE IN XMIN AND XMAX ON SAME LINE...
.11 .37
XMIN=   Ø.11ØØ XMAX=   Ø.37ØØ XDELTA=   Ø.3ØØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=   Ø.ØØØ2 YMAX=  1Ø.1297 YDELTA=   1.6882
TYPE IN YMIN AND YMAX ON SAME LINE...
Ø 12
YMIN=   Ø.ØØØØ YMAX=  12.ØØØØ YDELTA=   2.ØØØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
```

The screen will erase and plot Figure G-1. Hitting a carriage return:

```
DO YOU WANT A CALCOMP PLOT?
N

DO YOU WANT ANOTHER PLOT OPTION?
N

DO YOU WANT A VONK ANALYSIS OF THESE CURVES?
N

DO YOU WANT TO REFIT THE DATA?
Y    (a No will return the user to the Option section (3.2.2))

DO YOU WANT TO START WITH THE LAST "BEST" FIT PARAMETERS?
   (EXCEPT THE EXPONENTS WHICH WILL ALL BE SET TO 4.Ø)
```

(a No will return control to the entry of the background points)

(a Yes will start fitting immediately using the final parameters as the starting parameters. The exponents or Gaussian fractions will be reset to median values.)

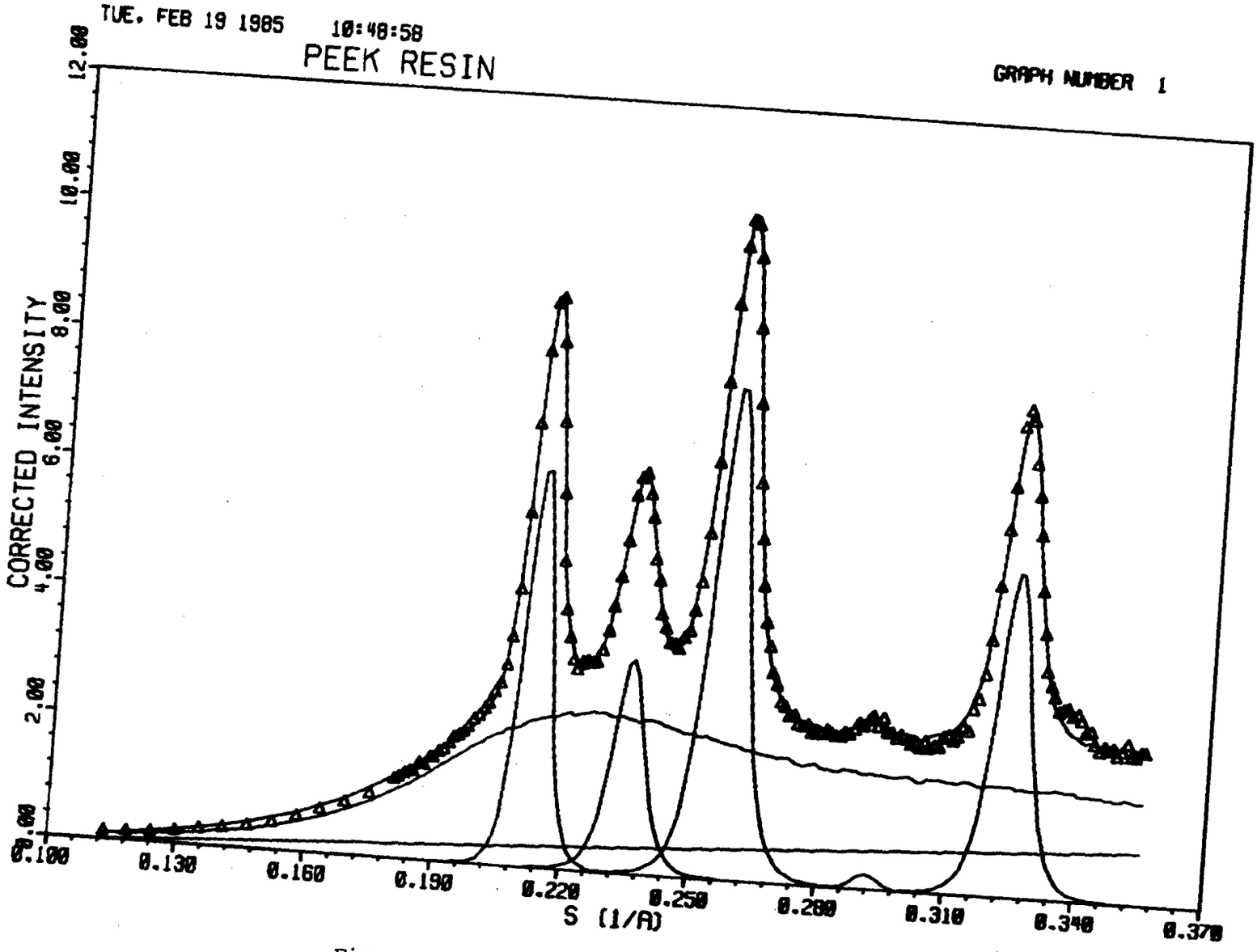

Figure G-1. Sample plot of fitted curves.

APPENDIX H

TYPICAL CURVE FITTING OUTPUT ON "FIT.PAR"

Written when the print option is 2 or 3.

```
ITERATION NUMBER   1

BASELINE POSITIONS AND INTENSITIES
Ø.1131   1 Ø.ØØØØØ
Ø.3554   Ø Ø.5ØØØØ

   PEAK POS      INT AT MAX      FW-HM      EXPONENT
Ø Ø.24Ø2Ø   Ø     2.5ØØØØ   Ø Ø.Ø8Ø81   1    -1.ØØ
Ø Ø.21ØØØ   Ø     5.ØØØØØ   Ø Ø.ØØ6ØØ   Ø     4.ØØ
Ø Ø.235ØØ   Ø     3.ØØØØØ   Ø Ø.ØØ7ØØ   Ø     4.ØØ
Ø Ø.257ØØ   Ø     7.ØØØØØ   Ø Ø.ØØ8ØØ   Ø     4.ØØ
Ø Ø.29ØØØ   Ø     Ø.5ØØØØ   Ø Ø.ØØ6ØØ   Ø     4.ØØ
Ø Ø.32ØØØ   Ø     4.ØØØØØ   Ø Ø.ØØ8ØØ   Ø     4.ØØ

ITERATION NUMBER   2

BASELINE POSITIONS AND INTENSITIES
Ø.1131   1 Ø.ØØØØØ
Ø.3554   Ø Ø.74527

   PEAK POS      INT AT MAX      FW-HM      EXPONENT
Ø Ø.24332   Ø     2.673Ø7   Ø Ø.Ø7819   1    -1.ØØ
Ø Ø.21193   Ø     4.79896   Ø Ø.ØØ843   Ø     1.ØØ
Ø Ø.235Ø6   Ø     3.29892   Ø Ø.ØØ8Ø5   Ø     1.ØØ
Ø Ø.25692   Ø     7.59731   Ø Ø.ØØ935   Ø     1.ØØ
Ø Ø.29Ø76   Ø     Ø.17393   Ø Ø.ØØ63Ø   Ø    3Ø.34
Ø Ø.32326   Ø     3.1376Ø   Ø Ø.Ø1167   Ø     1.ØØ

      .
      .
      .

ITERATION NUMBER  1Ø

BASELINE POSITIONS AND INTENSITIES
Ø.1131   1 Ø.ØØØØØ
Ø.3554   Ø Ø.77594

   PEAK POS      INT AT MAX      FW-HM      EXPONENT
Ø Ø.24229   Ø     2.5637Ø   Ø Ø.Ø8Ø55   1    -1.ØØ
Ø Ø.21243   Ø     6.23796   Ø Ø.ØØ755   Ø     3.88
Ø Ø.235Ø4   Ø     3.33638   Ø Ø.ØØ87Ø   Ø     2.79
Ø Ø.25691   Ø     7.67952   Ø Ø.ØØ97Ø   Ø     2.82
Ø Ø.2918Ø   Ø     Ø.25899   Ø Ø.ØØ6Ø3   1 5555.ØØ
Ø Ø.32419   Ø     5.12417   Ø Ø.ØØ922   Ø     2.76
```

APPENDIX I

TYPICAL CURVE FITTING OUTPUT ON "FIT.DAT"

Written when the print option is 2 or 3.

```
*********************************************************
* PEEK RESIN                                            *
*             WED, NOV 07 1984    09:55:18              *
*********************************************************
```

WEIGHT FACTOR=SQRT(Y(I)/YMAX)

THE FINAL FITTING PARAMETERS AND OTHER INFORMATION ARE GIVEN BELOW:

	PEAK POS	D-SPACING	INT AT MAX	AREA		FW-HM	INTGRL BRDTH	EXPONENT
AMOR	0	0.24229	4.12728	0	2.56370	0.74740	0	0.08055
0.29153	1	-1.00						
PK 1	0	0.21243	4.70733	0	6.23796	0.10652	0	0.00755
0.01708	0	3.88						
PK 2	0	0.23504	4.25457	0	3.33638	0.06756	0	0.00870
0.02025	0	2.79						
PK 3	0	0.25691	3.89242	0	7.67952	0.17313	0	0.00970
0.02254	0	2.82						
PK 4	0	0.29180	3.42706	0	0.25899	0.00332	0	0.00603
0.01283	1	5555.00						
PK 5	0	0.32419	3.08463	0	5.12417	0.11015	0	0.00922
0.02150	0	2.76						

BASELINE POSITIONS AND INTENSITIES

1	0.1131	1	0.00000
2	0.3554	0	0.77594

BASELINE AREA = 0.09401

(when space permits data from each angle will all be on a single line)

TWO THETA	S (1/A)	++++ INTENSITIES ++++ OBS	CALC	OBS-CALC	BASELINE	INDIVIDUAL AMORPHOUS	PEAKS PK 1	PK 2	PK 3	PK 4	PK 5
10.00	0.1131	0.141	0.100	0.041	0.000	0.100	0.000	0.000	0.000	0.000	0.000
10.50	0.1187	0.158	0.128	0.030	0.018	0.110	0.000	0.000	0.000	0.000	0.000
11.00	0.1243	0.184	0.173	0.011	0.036	0.137	0.000	0.000	0.000	0.000	0.000
11.50	0.1300	0.229	0.220	0.008	0.054	0.166	0.000	0.000	0.000	0.000	0.000

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19.50	0.2197	3.649	3.654	-0.006	0.341	2.500
0.761	0.049	0.002	0.000	0.000		
19.60	0.2208	3.308	3.393	-0.086	0.345	2.518
0.459	0.068	0.003	0.000	0.000		
19.70	0.2219	3.169	3.212	-0.043	0.349	2.488
0.277	0.095	0.003	0.000	0.000		
19.80	0.2230	3.276	3.166	0.111	0.352	2.506
0.168	0.135	0.004	0.000	0.000		
19.90	0.2241	3.293	3.172	0.122	0.356	2.514
0.103	0.194	0.005	0.000	0.000		
20.00	0.2253	3.281	3.251	0.030	0.359	2.542
0.064	0.280	0.006	0.000	0.000		
20.10	0.2264	3.301	3.374	-0.073	0.363	2.555
0.040	0.409	0.007	0.000	0.000		
20.20	0.2275	3.473	3.547	-0.074	0.366	2.549
0.026	0.598	0.008	0.000	0.000		
20.30	0.2286	3.776	3.823	-0.047	0.370	2.556
0.017	0.869	0.010	0.000	0.000		
20.40	0.2297	4.157	4.188	-0.031	0.374	2.545
0.011	1.245	0.012	0.000	0.000		
20.50	0.2308	4.622	4.642	-0.020	0.377	2.510
0.008	1.731	0.015	0.000	0.000		
20.60	0.2319	5.187	5.206	-0.019	0.381	2.506
0.005	2.295	0.019	0.000	0.000		
20.70	0.2331	5.886	5.780	0.105	0.384	2.525
0.004	2.843	0.024	0.000	0.000		
20.80	0.2342	6.162	6.146	0.016	0.388	2.494
0.003	3.232	0.030	0.000	0.000		
20.90	0.2353	6.243	6.249	-0.005	0.391	2.489
0.002	3.329	0.038	0.000	0.000		
21.00	0.2364	5.918	5.995	-0.077	0.395	2.454
0.001	3.096	0.049	0.000	0.000		
21.10	0.2375	5.562	5.532	0.030	0.399	2.448
0.001	2.620	0.064	0.000	0.000		
21.20	0.2386	4.925	5.010	-0.086	0.402	2.474
0.001	2.050	0.083	0.000	0.000		
21.30	0.2397	4.602	4.504	0.097	0.406	2.475
0.001	1.513	0.110	0.000	0.000		

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31.50	0.3521	2.350	2.435	-0.085	0.765	1.663
0.000	0.000	0.000	0.000	0.006		
31.60	0.3532	2.348	2.426	-0.078	0.769	1.652
0.000	0.000	0.000	0.000	0.005		
31.70	0.3543	2.411	2.415	-0.004	0.772	1.638
0.000	0.000	0.000	0.000	0.004		
31.80	0.3554	2.411	2.423	-0.012	0.776	1.643
0.000	0.000	0.000	0.000	0.004		

APPENDIX J

EXAMPLE OF SIMPLE INTEGRAL LINE BREADTH

Enter Option 5 and after the screen erases:

```
DO YOU WANT SIMPLE INTEGRAL BREADTH (S), OR
   WILSONS VARIANCE METHOD (DEFAULT) OF LINE BREADTH?
S
DO YOU WANT A BASELINE?  Y/N
Y                                       (default)
DO YOU WANT CONSTANT INTENSITY CORRECTION?  Y/N
N                                       (default)
                                        Straight line background
TYPE IN THMIN AND THMAX FOR PEAK AREA
18 22
INTEGRAL LINE BREADTH= Ø.9593 DEGREES TWO THETA.
 INTEGRATED OVER 18.ØØ TO  21.8Ø DEGREES TWO THETA.
 THE MAXIMUM INTENSITY=  1234.321

DO YOU WANT TO TRY ANOTHER PEAK?  Y/N
Y
DO YOU WANT A BASELINE?  Y/N
Y                                       (default)
DO YOU WANT CONSTANT INTENSITY CORRECTION?  Y/N
Y
TYPE IN INTENSITY CORRECTION
12.                                     Constant background
TYPE IN THMIN AND THMAX FOR PEAK AREA
18 22
INTEGRAL LINE BREADTH= Ø.95ØØ DEGREES TWO THETA.
 INTEGRATED OVER 18.ØØ TO  21.8Ø DEGREES TWO THETA.
 THE MAXIMUM INTENSITY=  1234.321

DO YOU WANT TO TRY ANOTHER PEAK?  Y/N
Y
DO YOU WANT A BASELINE?  Y/N
N                                       No background correction
TYPE IN THMIN AND THMAX FOR PEAK AREA
18 22
INTEGRAL LINE BREADTH= Ø.9432 DEGREES TWO THETA.
 INTEGRATED OVER 18.ØØ TO  21.8Ø DEGREES TWO THETA.
 THE MAXIMUM INTENSITY=  1234.321

DO YOU WANT TO TRY ANOTHER PEAK?  Y/N
N
```

Return to Main program Option section (3.2.2)

APPENDIX K

WILSON'S VARIANCE METHOD FOR LINE BREADTH

Enter Option 5 and after the screen erases:

```
DO YOU WANT SIMPLE INTEGRAL BREADTH (S), OR
   WILSONS VARIANCE METHOD (DEFAULT) OF LINE BREADTH?
                  default

ENTER INITIAL AND FINAL TWO-THETA RANGE FOR PEAK
27.2 31

INITIAL AVERAGE BACKGROUND = 33.5370
THE CENTROID OF THE PEAK IS LOCATED AT :  29.122
   THE OLD LIMITS WERE :  27.200  TO  31.000
   THE NEW LIMITS ARE  :  27.244  TO  31.000

MINIMUM BACKGROUND IS  3.7411

 **  WAIT  **

MAXIMUM BACKGROUND IS 37.4112

MINIMUM ERROR OCCURS WITH A BACKGROUND OF 33.6701
   DO YOU WANT A PLOT OF THESE VARIANCES (Y) OR
   DO YOU WANT TO TRY OTHER BACKGROUNDS (N) ?
Y
```

The screen erases and Figure K-1 will be plotted. At the end of the plot the minimum error line is repeated and then (or if N had been the above answer) the program continues:

```
ENTER DESIRED AVERAGE BACKGROUND AND BKG INCREMENT
   TO TERMINATE THIS LOOP ENTER "0" INCREMENT
32. .5

MINIMUM BACKGROUND IS 30.0000

 **  WAIT  **

MAXIMUM BACKGROUND IS 34.5000

MINIMUM ERROR OCCURS WITH A BACKGROUND OF 32.5000
   DO YOU WANT A PLOT OF THESE VARIANCES (Y) OR
   DO YOU WANT TO TRY OTHER BACKGROUNDS (N) ?
N
```

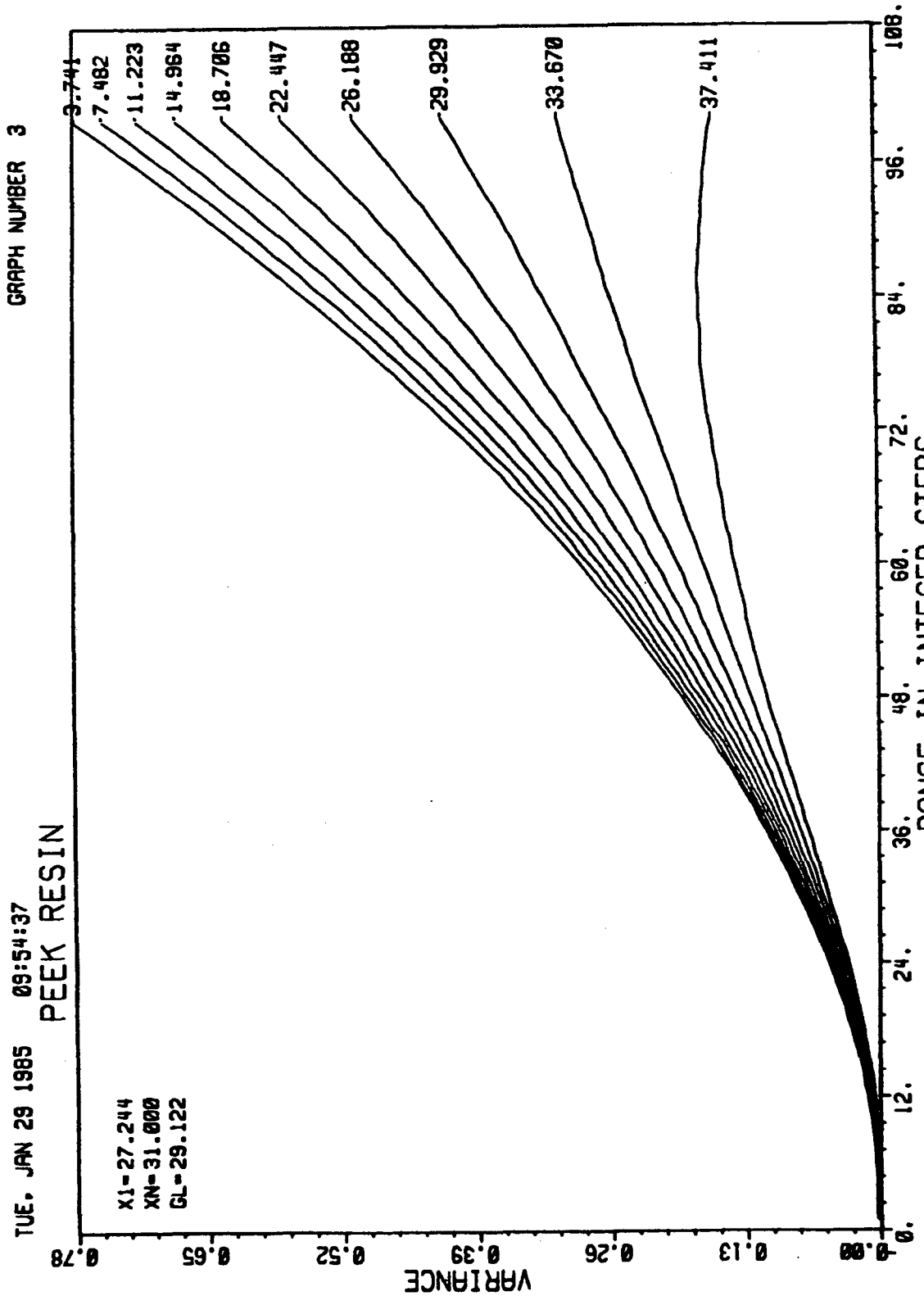

Figure K-1. Variance versus range curves for a family of backgrounds.

```
ENTER DESIRED AVERAGE BACKGROUND AND BKG INCREMENT
   TO TERMINATE THIS LOOP ENTER "Ø" INCREMENT
32.5 Ø.

XMIN=   Ø.Ø256 XMAX=   1.8997 XDELTA=   Ø.2Ø83
TYPE IN XMIN AND XMAX ON SAME LINE...
Ø 2.25
XMIN=   Ø.ØØØØ XMAX=   2.25ØØ XDELTA=   Ø.25ØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
YMIN=  -Ø.ØØ11 YMAX=   Ø.3567 YDELTA=   Ø.Ø593
-.15 .45
YMIN=  -Ø.15ØØ YMAX=   Ø.45ØØ YDELTA=   Ø.1ØØØ
DO YOU WISH TO CHANGE THESE?  Y/N
N
```

The screen erases and Figure K-2 is plotted. The straight least squares line is drawn automatically and the user has an opportunity to get a hard copy of the plot before the slope and intercept information is printed as in Figure K-2. When the single background plot is complete the program will list the available options within the Wilson's variance Option as explained in the Operations section (3.2.6)

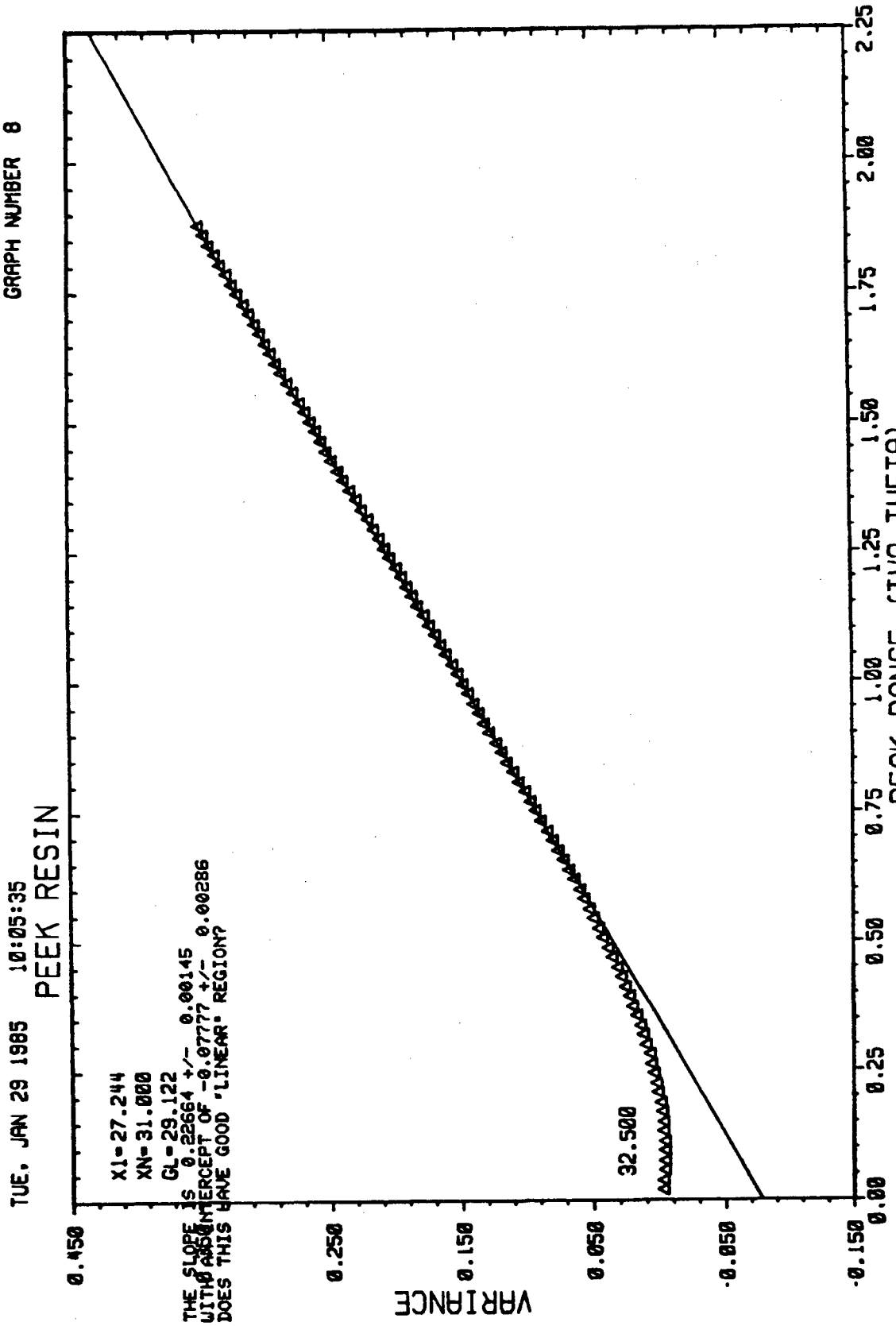

Figure K-2. Variance-range curve with a least squares line through the linear portion.

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